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A STUDY OF THE REMOVAL OF PESTICIDES FROM WATER

KENTUCKY WATER RESOURCES INSTITUTE

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A STUDY OF THE REMOVAL OF PESTICIDES FROM WATER

By

JAMES DAVID WHITEHOUSE

1967

UNIVERSITY OF KENTUCKY
WATER RESOURCES INSTITUTE
LEXINGTON, KENTUCKY

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Whitehouse, J. D.

9. Kentucky University, Lexington, Water
Resources Research Institute

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The removal of pesticides from water by aeration was [redacted] significant. Dieldrin was removed almost 100 percent, while aldrin, DDT, and BHC were removed to a lesser extent. There was no loss of 2,4,5-T and captan ~~showed no loss~~ through aeration.

Chemical coagulation alone was [redacted] ineffective in the removal of pesticides from water. Several coagulant aids were investigated but all proved ineffective with the possible exception of one which increased the apparent removal slightly.

Of the processes investigated adsorption with activated carbon was ~~determined to be~~ the most effective in removing pesticides from water. The removals obtained were--malathion near 100 percent; 2,4-D, 90 percent; DDT, 95 percent; aldrin, 100 percent; dieldrin 90 percent. [(Huffsey-Kentucky)]

*Pesticide Removal, *Pesticides, *Water treatment, *Aeration, Adsorption, Foam separation, *Waste water treatment Pesticide residues, *Activated carbon, Clays, DDT, Coagulation, 2,4-D, Aldrin, Dieldrin, 2,4,5-T.

Chemical coagulation, Malathion, Captan, Benzene haxachloride

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Research Report No. 8

UNIVERSITY OF KENTUCKY
WATER RESOURCES INSTITUTE

A STUDY OF THE REMOVAL OF PESTICIDES FROM WATER

James David Whitehouse

The work on which this report was based was supported in part by the U. S. Public Health Service, Division of Water Supply and Pollution Control (now the Federal Water Pollution Control Administration, Department of the Interior) under Contract No. WP-00476-02; and in part by the U. S. Department of the Interior, Office of Water Resources Research, under Contract No. 14-01-0001-911.

December, 1967

ABSTRACT

The purpose of this study was to investigate some of the properties of pesticides as they exist in water, and to determine the effectiveness of several water treatment processes in the removal of pesticides from water. Among the pesticides investigated were malathion, DDT, aldrin, dieldrin, captan, benzene hexachloride (BHC), 2,4-D, and 2,4,5-T. The water treatment processes included aeration, chemical coagulation, adsorption on activated carbons and clays, and foam separation.

The removal of pesticides from water by aeration was found to be significant. Dieldrin was removed almost 100 percent, while aldrin, DDT, and BHC were removed to a lesser extent. 2,4,5-T and captan showed no loss through aeration.

Chemical coagulation alone was found to be ineffective in the removal of pesticides from water. Several coagulant aids were investigated but all proved ineffective with the possible exception of one which increased the apparent removal slightly.

Of the processes investigated adsorption with activated carbon was determined to be the most effective in removing pesticides from water. The removals obtained were -- malathion near 100 percent; 2,4-D, 90 percent; DDT, 95 percent; aldrin, near 100 percent; dieldrin, 90 percent.

Studies on the removal of aldrin and dieldrin from water by the use of surface active agents to produce a foam demonstrated that this process might be of value as a treatment method, with removals greater than 90 percent being achieved in some cases.

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CHAPTER I

INTRODUCTION

For many years there has been a growing concern that the uncontrolled use of pesticides would have harmful effects on man's environment. Since the development of the synthetic pesticides during World War II, the use of these compounds has increased some fifteen fold. With this increase in the use of pesticides and the increased exposure of man to them, the evaluation of the effects of pesticides on the environment becomes more urgent.

This report is concerned with the presentation of data which has been obtained on some of the properties of pesticides as they exist in water and their removal from water by water treatment processes. Among the pesticides investigated were malathion, DDT, aldrin, dieldrin, captan, benzene hexachloride (BHC), 2,4-D, and 2,4,5-T. The water treatment process included aeration, coagulation with alum, adsorption on activated carbons and clays, and foam separation.

PHYSICAL AND CHEMICAL PROPERTIES OF THE SYNTHETIC ORGANIC PESTICIDES USED

Chlorinated Hydrocarbons

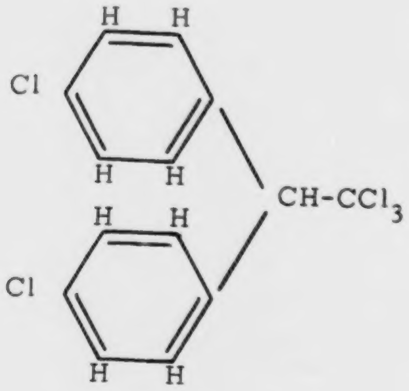
The DDT Series. The major compounds of the DDT Series are DDT (dichloro-diphenyl-trichloroethane), DDD (dichloro-diphenyl-dichloroethane) and methoxychlor.

DDT - Dichlorodiphenyltrichloroethane ($C_{14}H_9Cl_5$)

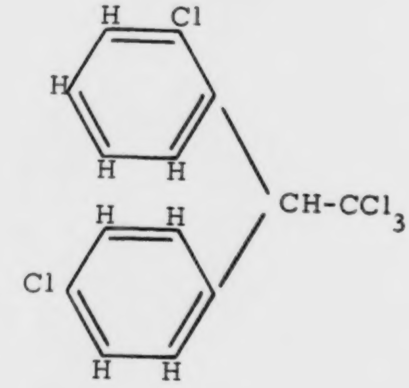
The compound known as DDT was first synthesized in 1874 by Zeidler. He did not realize the insecticidal properties of the compound he had developed, and it was not until some fifty years later that Swiss entomologists found DDT to be a surprisingly good insecticide. It was patented in the U. S. in 1943 (patent No. 2,329,074) (2).

The compound DDT can exist in a number of isomeric forms depending on the position of the substituted chlorine atom. The para-para' isomer, 2,2-bis(p-chlorophenyl) -1,1,1-trichloroethane, makes up about 70% of the technical grade of DDT, the ortho-para' isomer makes up 10 to 15%, with the remainder being related compounds and impurities. The p, p' - isomer melts at 108.5 - 109.0 C, the o, p' - isomer at 74.0 - 74.5° C, and the o, o' - isomer at 92.0 - 93.0° C (4) (Figure 1-1).

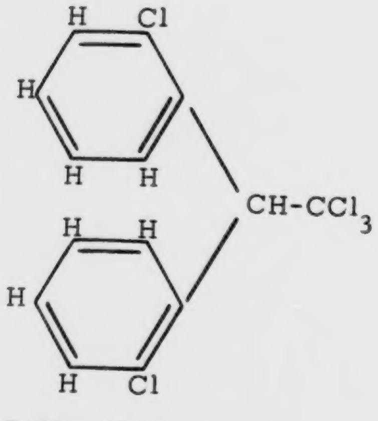
As stated technical DDT contains approximately 70% of p, p' - DDT which is the most active insecticidal principal.


H
H
Cl
H
H
CH-CCl3
H
H
Cl
H
H

P,P' - Isomer


H
Cl
H
H
H
CH-CCl3
H
H
Cl
H
H

0,P' - Isomer


H
Cl
H
H
H
CH-CCl3
H
H
H
H
Cl

0,0' - Isomer

Figure 1-1

ISOMERS OF DDT (3)

Haller and his associates in their examination of three samples of technical DDT found thirteen other compounds. Some of these were undoubtedly present as impurities in the technical chloral and chlorobenzene used in the reaction and the others products of side reactions. Some of these had insecticidal properties but none were equivalent to the p, p' - DDT in toxicity (Table 1-1) (2).

Technical DDT is formed by reacting chloral with chlorobenzene in the presence of sulfuric acid as shown in Figure 1-2 (3). Technical DDT contains 9 5 - 11% hydrolyzable chlorine and 1% volatile and alcohol insoluble material. It has a minimum setting point of 89°C and is composed of at least thirteen compounds which are listed in Table 1-1. Chemically pure p, p' - DDT is a stable, white, crystalline material, only slightly volatile, having a boiling point of 185°/1mm, density of 1.6, and a vapor pressure of 1.5 x 10^{-7} mm of Hg @ 20° C (3).

Technical DDT is soluble in organic solvents @ 27-30° C as shown below (in grams per 100 ml. of solvent), but is only slightly soluble in water.

Acetone	58
Benzene	78
Carbon tetrachloride	45
Ethyl alcohol	28
Dioxane	100

DDT is dehydrochlorinated by alcoholic alkali to form DDE

TABLE 1-1

APPROXIMATE COMPOSITION OF TECHNICAL DDT (2)

Compound	Approximate Percentage
1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane (p,p'-DDT)	63-77
1,1,1-Trichloro-2-(o-chlorophenyl-2-(p-chlorophenyl) ethane (o,p'-DDT)	8-21
1,1-Dichloro-2,2-bis(p-chlorophenyl) ethane (p,p'-TDE)	0.3-4.0
1,1-Dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethane (o,p'-TDE)	0.04
1-o-Chlorophenylethyl-2-trichloro-p-chlorobenzene sulfonate	0.1-1.9
2-Trichloro-1-p-chlorophenylethanol	0.2
Bis(p-chlorophenyl) sulfone	0.03-0.6
α-Chloro-α-p-chlorophenylacetamide	0.01
α-Chloro-α-o-chlorophenylacetamide	0.01
Chlorobenzene	0.3
p-Dichlorobenzene	0.1
1,1,1,2-Tetrachloro-2-(p-chlorophenyl) ethane	present
Sodium p-chlorobenzenesulfonate	0.02
Ammonium p-chlorobenzenesulfonate	0.01
Inorganic	0.01-0.1
Unidentified and losses	5.1-10.6

Data approximated from analyses of 3 samples by Hallen (2), et.al. Figures represent roughly the ranges found.

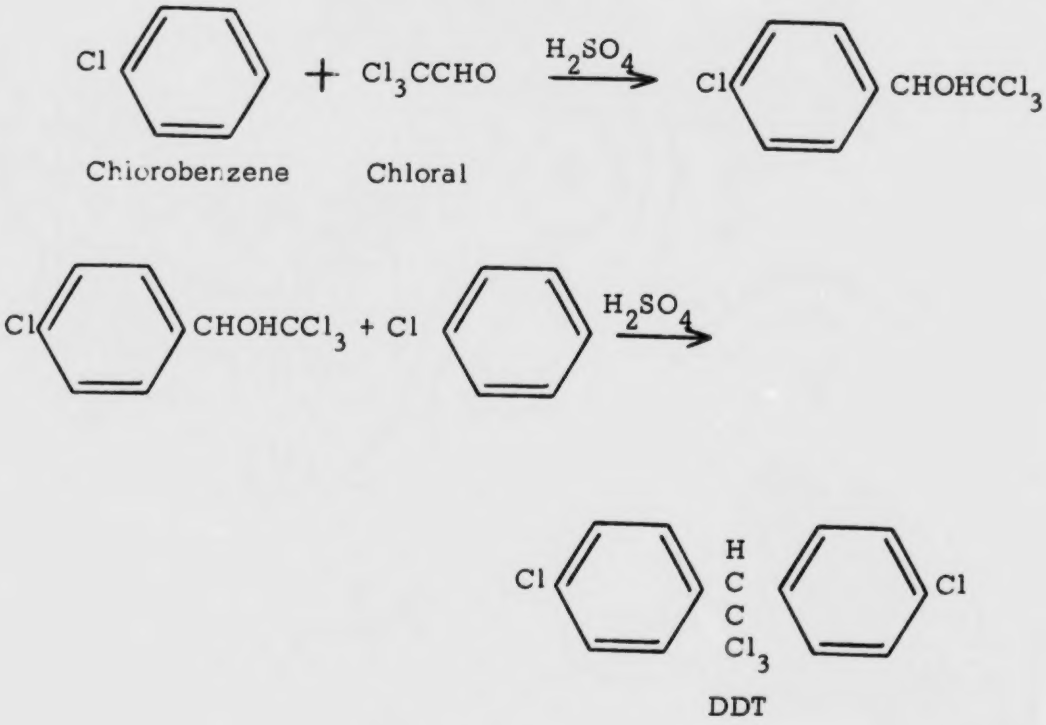
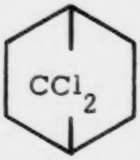

Cl
Cl$_3$CCHO
H_2SO_4
Cl
CHOHCCl$_3$
Chlorobenzene
Chloral
Cl
CHOHCCl$_3$ + Cl
H_2SO_4
Cl
H
C
C
Cl$_3$
Cl
DDT

Figure 1-2

PREPARATION OF DDT (3)

(2,2-bis-p-chlorophenyl) - 1,1-dichloroethylene), which has a melting point 88-89°C. This reaction is catalyzed by traces of iron, aluminum, and chromium salts. Under field conditions and exposed to ultraviolet irradiation, DDT is slowly decomposed into noninsecticidal components. The reactions that are believed to be involved in the decomposition are shown in Figure 1-3.

The Chlordane Series. This group of insecticides is known as the cyclodiene insecticides and includes chlordane, heptachlor, aldrin, dieldrin, isodrin, endrin, and toxaphene. These are all highly chlorinated cyclic hydrocarbons with the characteristic "endomethylene bridge" structure. They are, except for toxaphene, produced by the well-known Diels-Alder condensation reaction, and were discovered and developed around 1945 (3).



ENDOMETHYLENE BRIDGE

Chlordane

Chlordane (U.S. Patent No. 2,519,190) was first made by

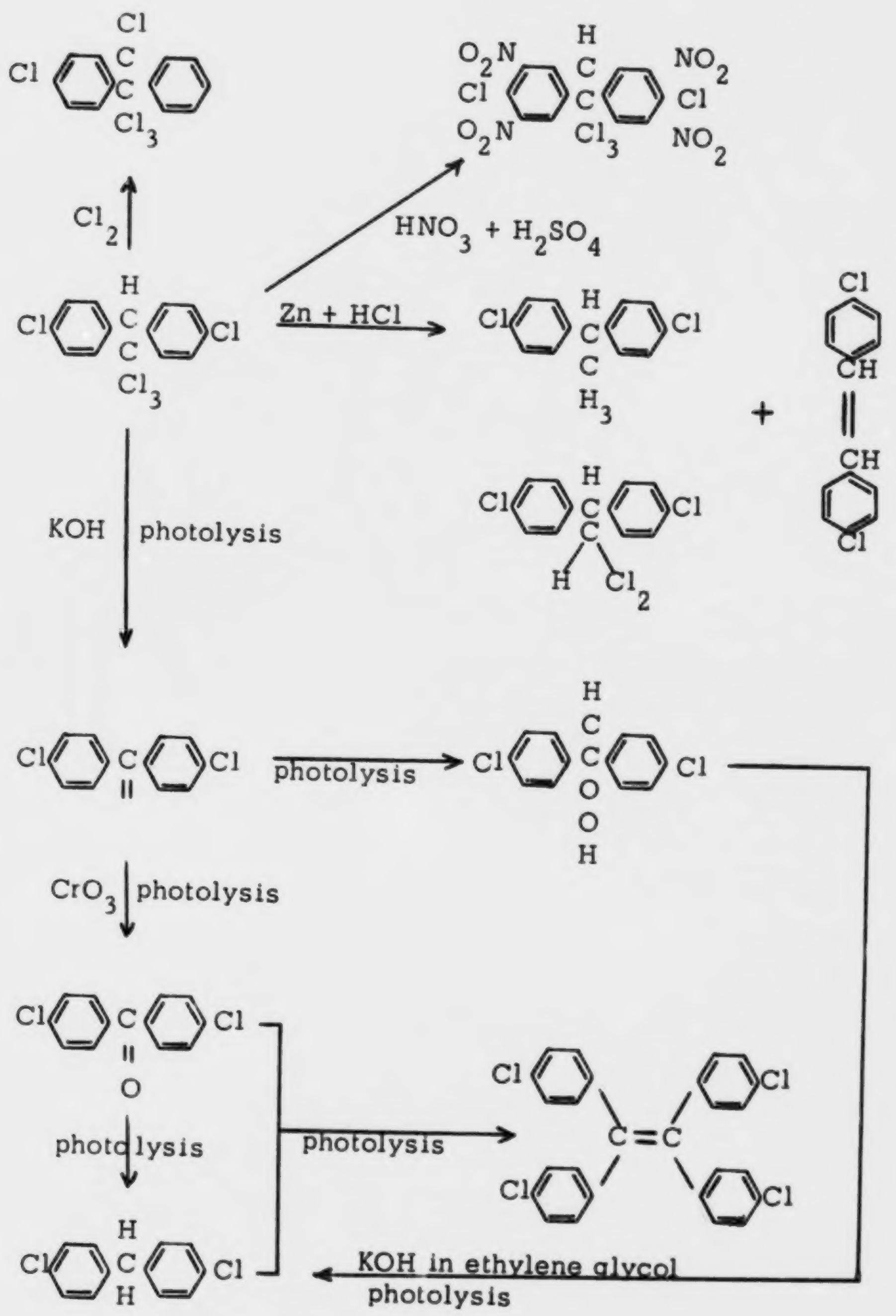

Cl2
HNO3 + H2SO4
Zn + HCl
KOH
photolysis
CrO3
KOH in ethylene glycol

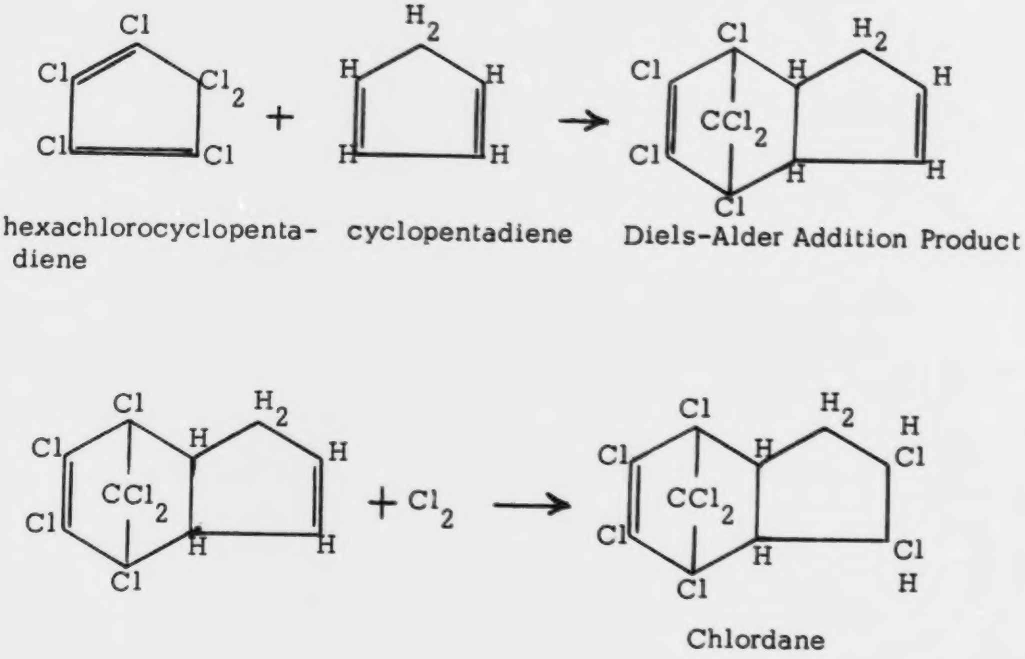
Figure 1-3

DECOMPOSITION OF DDT (3)

Hyman and announced by Kearns et.al. in 1945. A compound identical with chlordane was claimed to have been discovered by Reimschneider and Kuhnl at about the same time (2).

Chlordane is prepared (Figure 1-4) when hexachlorocyclopentadiene is combined with cyclopentadiene forming a Diels-Alder addition product. The addition product is then dissolved in carbon tetrachloride and treated with chlorine, which breaks the double bond on the five-membered ring allowing the chlorine atom to be added, forming chlordane (2). Chlordane chemically is 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan (2). The technical product contains 60 to 75 percent of the pure compound and 25 to 40 percent of related compounds (1). It is a dark brown viscous liquid with a cedar-like odor, with a density @ 25°C of 1.61, and a boiling point of 175°C @ 2mm.Hg. When refined, the product is a pale yellow with a vapor pressure of 1×10^{-5} mm.Hg (3) and a refractive index of 1.56-1.57 @ 25°C (2).

Technical chlordane is completely soluble in the aromatic and aliphatic hydrocarbons, esters, ethers, ketones etc. and only very slightly soluble in water. When exposed to alkali it readily loses hydrogen chloride to form nontoxic products, and this reaction is catalyzed by traces of iron. The technical grade chlordane is a mixture of several compounds of varying degrees



Cl
Cl
Cl2
Cl
Cl
+
H2
H
H
H
H
Cl
H2
Cl
H
H
CCl2
Cl
H
H
Cl
hexachlorocyclopentadiene
cyclopentadiene
Diels-Alder Addition Product
Cl
H2
Cl
H
H
CCl2
Cl
H
H
Cl
+ Cl2
Cl
H2
H
Cl
H
Cl
CCl2
Cl
H
Cl
Cl
H
Chlordane

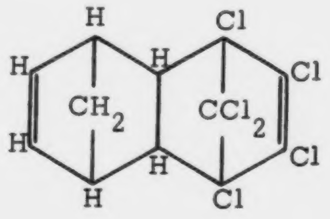
Figure 1-4

PREPARATION OF CHLORDANE (2)

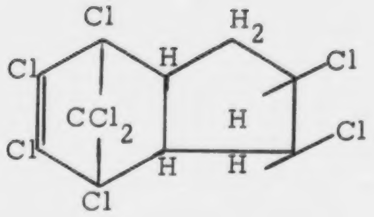
of physiological activity (3).

There has been some discussion as to the number of isomers of chlordane ($C_{10}H_6Cl_8$). Riemschneider has claimed the existence of 5 isomers m.p. 101-3°, 102-4°, 81-84°, 137-139° and 73°C. March has separated three and Vogelbach claims the existence of eight possible stereoisomers (3). It was shown by Cristol that in 0.04 M ethanolic sodium hydroxide, β-chlordane readily dehydrochlorinates, while α-chlorodane is inert, suggesting that β-chlordane has a cis-configuration (Figure 1-5) (3). The heptachloro-compound is fairly stable under these conditions while the enneachloro-compound reacts readily. Although conclusive evidence has not been presented it is believed that the heptachloro-, octachloro-, and enneachloro-compounds are in the endo - rather than exo - forms (3).

Aldrin. (hexachlorohexahydro-endo, exo-dimethanonaphtalene); (HHDN), aldrin is defined as containing 95% HHDN and 5% of insecticidally active related compounds.

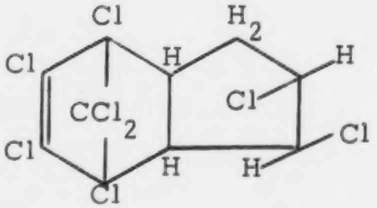


ALDRIN


Cl
H_2
Cl
H
Cl
CCl_2
H
Cl
Cl
H
H
Cl

1,2,4,5,6,7,8,8-Octachloro-
2,3,3a,4,7,7a-hexahydro-
4,7-methanoindene
(M.P. 102-104°C)

Chlordane - Cis Isomer


Cl
H_2
Cl
H
H
Cl
CCl_2
Cl
Cl
H
H
Cl

1,2,4,5,6,7,8,8-Octachloro-
2,3,3a,4,7,7a-hexahydro-
4,7-methanoindene
(M.P. 104-106°C)

Chlordane - Trans Isomer

Figure 1-5

A new insecticide "compound 118" was announced and became available in 1948. In 1949 Kearns, Weinman, and Decker published the first tests on the new insecticide. This compound is covered by U. S. Patent 2,635,977 and was later assigned the name of aldrin, chosen because it was made by the Diels-Alder reaction. Dieldrin was also named at the same time for the same reason. Pure aldrin is a white, crystalline solid without appreciable odor at room temperature. It melts at 104-104.5°C, and at temperatures above room temperature has a mild pine-like odor. It is very slightly soluble in water and is soluble in organic solvents at 30°C as given below, expressed as grams of aldrin per 100 ml of solvent (2):

Methanol	9
White Kerosene	89
Hexane	98
Acetone	159
Benzene	350

Technical aldrin is a soft solid containing not less than 77.9% HHDN. It is a tan to dark brown in color, without corrosive action, nonflammable, and stable in many of the organic and inorganic bases and alkaline oxidizing agents. It reacts with concentrated mineral acids, oxidizing agents, phenols and active metals (1).

Structural isomers (endo and exo-forms) are possible in the bridged-ring compound 1,2,3,4,10,10-hexachloro-1,4,4a,5,8, 8a-hexahydro-1,4,5,8-dimethanonaphthalene. The active principal of aldrin is the endo-exo-isomer. The names of these isomers are based on the relative positions occupied by the two rings in relation to each other (2). Looking at one ring at a time, attachments can be made in two positions. Carbon atoms labeled 7 in Figure 1-6 at the top of the structure are the bridge or "methano-" carbons. Rings attached to carbons 1 and 2 may be in two positions, as shown in Figure (a). They lie outside an angle which can be drawn from the bridge carbon to the outside "corner" carbon atom (angle is shown by dotted lines): These are termed exo derivatives. Rings attached as shown in Figure (b) which lie within the angle are named endo derivatives (2). The second ring may also have attachments which can be exo or endo, therefore four theoretical isomers may exist.

Aldrin is stable chemically and is not decomposed by alkaline materials, and under practical conditions it is unaffected by acidic reagents. Oxidation of aldrin under field conditions yields the epoxide derivative that is the active principal of dieldrin (2).

Aldrin is highly toxic initially but does not exhibit a long lasting residual action. As normally used, it is not phytotoxic.

Dieldrin. Dieldrin was first described by Kearns in 1948 under the name of "Compound 497" and is covered by Patent 2,676,131.

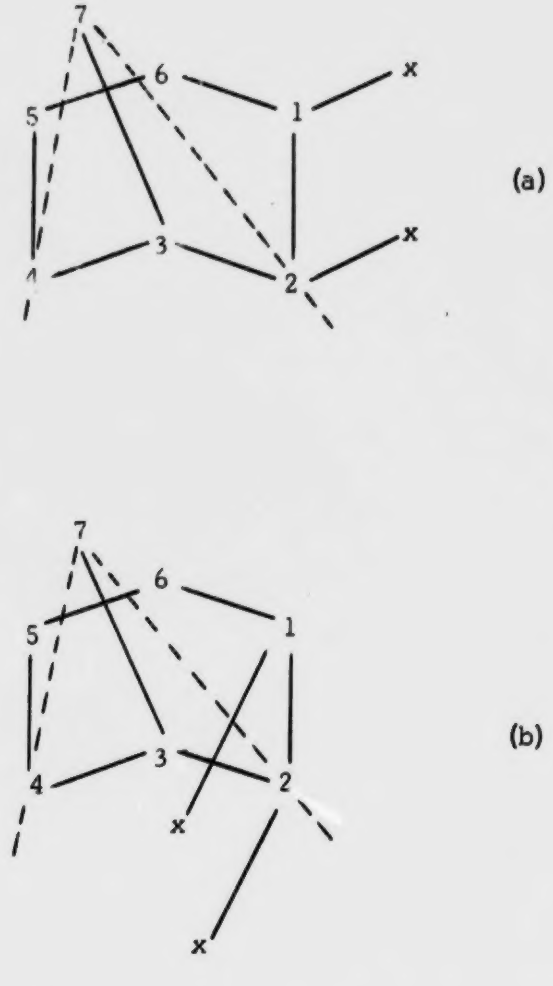

7
6
5
1
x
x
4
3
2
(a)
7
6
5
1
4
3
2
x
x
(b)

Figure 1-6

ENDO AND EXO-FORMS OF ALDRIN (2)

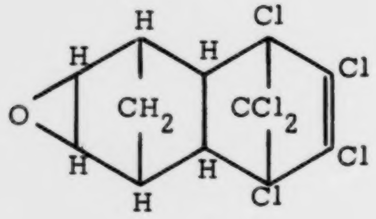
The name dieldrin was registered as a generic name in 1949 with the Patent Office. Dieldrin was so named, as was aldrin, because the compound is made by the Diels-Alder condensation reaction (2).

The principal constituent of dieldrin (hexachloroepoxyoctahydro-endo- exo-dimethano-naphthalene) is known as HEOD. Pure dieldrin contains 85 percent HEOD and 15 percent insecticidally active related compounds. It is a dry crystalline solid with a melting point of 175° - 176°C. Technical grade dieldrin is a light brown or tan flake with a setting point of 95°C minimum, vapor pressure 1.8×10^{-7} mm Hg at 25°C, noncombustible compound. It possesses a mild odor and is noncorrosive at room temperature (1).

Dieldrin is only slightly soluble in water, but soluble in organic solvents as listed below, expressed as grams of dieldrin per 100 grams of solvent @ 26°C (2).

Methanol	4.9
Acetone	54.0
Benzene	75.0
Hexane	7.7
Deodorized Kerosene	4.3

Dieldrin, chemically 1,2,3,4,10,10-hexochloro-6,7-epoxy-1,4,4a, 5,6,7,8,8a-octahydro-1,4,5,8-endo, exo-dimenthanonaphtalene, is a relative stable compound. Under normal conditions of use dieldrin is not decomposed by mineral acids or alkalies, and therefore may be formulated with a wide variety of other pesticides (2).



DIELDRIN (2)

Formation of aldrin and dieldrin, Figure 1-7, is by the Diels-Alder reaction between cyclopentadiene and acetylene to form bicyclo-[2.2.1] - 2,5-heptadiene which is then reacted with hexachlorocyclopentadiene to form aldrin. To form dieldrin, aldrin is reacted with peracetic or perbenzoic acid (3).

Dieldrin can be converted to aldrin by treatment with acetic and hydrobromic acids (3).

The Phenoxy Series. This group of the chlorinated hydrocarbons consists mainly of 2,4-D and 2,4,5-T.

(2,4-D) 2,4-Dichlorophenoxyacetic Acid

Investigators at the Boyce Thompson Institute for Plant Research conducted research on plant hormones for many years (2), and in 1943 U. S. Patent 2,322,760 was issued to cover the growth-stimulating properties of 2,4-D. In the patent, users were

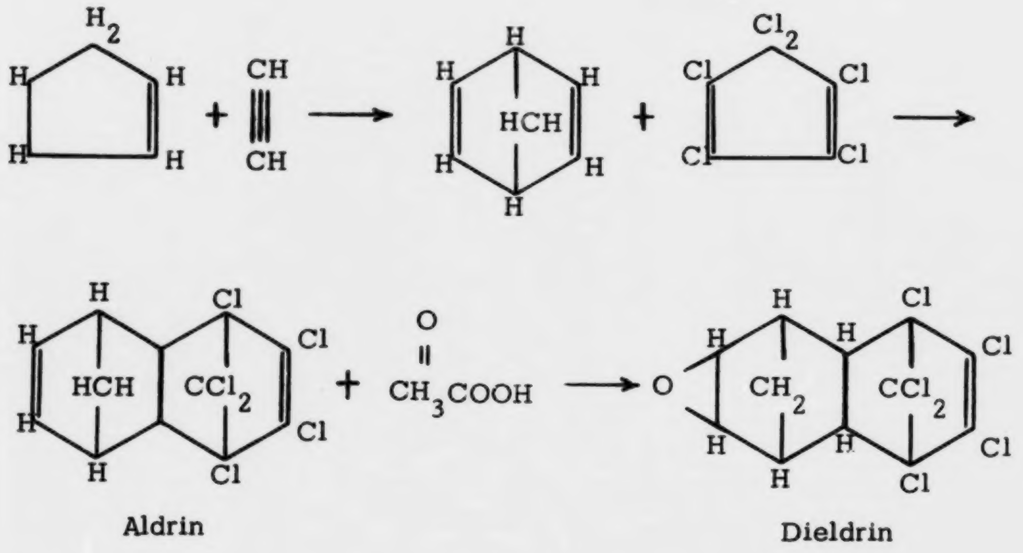

H2
H
H
H
H
CH
CH
H
H
HCH
H
H
H
H
Cl2
Cl
Cl
Cl
Cl
H
H
H
HCH
H
Cl
Cl
CCl2
Cl
Cl
O
CH3COOH
O
H
H
CH2
H
H
H
H
Cl
Cl
CCl2
Cl
Cl
Aldrin
Dieldrin

Figure 1-7

PREPARATION OF DIELDRIN AND ALDRIN (3)

cautioned against using high concentrations of 2,4-D because of its phytocidal properties which were not clearly understood at that time. Research was continued on 2,4-D and related compounds in this country and in England. For military reasons, the herbicidal properties of this compound were not disclosed promptly, but in 1945 U. S. Patent 2,390,941 was issued covering the herbicidal use of the halogenated phenoxyacetic acids and their derivatives as herbicides (2).

2,4-D may be prepared by condensing sodium 2,4-dichlorphenate and chloroacetic acid (Figure 1-8) (2). In its pure state 2,4-D is a white power that has a melting point of 138°C. It is corrosive and it reacts with metals and bases (1). It is stable under common storage conditions, and is only slightly soluble in water and oils. It is soluble in alcohols and is freely soluble in alkaline solutions, through the formation of soluble salts (3).

2,4-D as such is not used as a herbicide, but is the base material from which the various derivatives such as esters and salts are produced. Because of the very low solubility of 2,4-D, water soluble salts were prepared for convenience in application. One of the earliest salts used, the sodium salt, may be prepared by reacting the free acid with sodium hydroxide or sodium carbonate. This inorganic salt of 2,4-D is soluble in water to

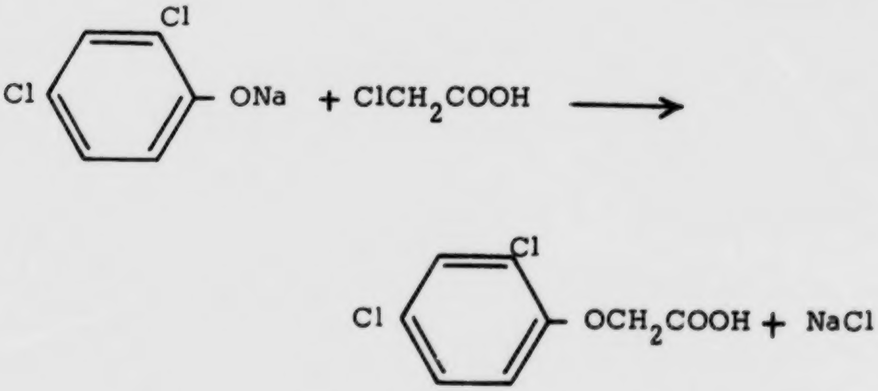


Figure 1-8

PREPARATION OF 2,4-D (2)

the extent of approximately 3.5 percent. Since the introduction of "low volume" spraying methods, in which only a few gallons of spray per acre are applied, the limited solubility of the sodium salt has proven to be a disadvantage. The amine salts and esters of 2,4-D, being more soluble, have largely replaced the inorganic salts (2).

The amines such as di-and trimethylamines, triethylamine, isopropylamine, di- and triethanol-amines, 2-propanolamine, and mixed alkanolamines, because of their alkaline nature, readily form salts with 2,4-D (2). These amine salts of 2,4-D are readily soluble in water and are therefore well adapted to agricultural use. The following amounts of amines required to form salts with 2,4-D acid were reported by Kelly (2).

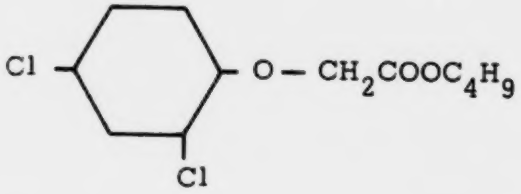
Weights of Technical Amines Required to Form Salts with 2,4-D (2)

Amine	Pounds of Amine per pound of 2,4-D
Dimethylamine $(CH_3)_2NH$	0.21
Isopropylamine $C_2H_5NH_2CH_3$	0.27
Triethylamine $(C_2H_5)_3N$	0.46
Diethanolamine $(HOC_2H_4)_2NH$	0.48
Triethanolamine $(HOC_2H_4)_3N$	0.64

As can be seen from these figures, it is apparent that the lower alkyl amines are the most economical materials to use in formulating

2,4-D amine salts, on the basis of equivalent weights. The amine salts of 2,4-D have a tendency to react with calcium and magnesium salts in hard water, which may cause clogging of equipment used in spraying. To alleviate this problem most of the present-day amine 2,4-D formulations contain sequestering agents or other compounds to form complexes with the salts present in hard waters. Amine salts of 2,4-D are not as toxic to plants as the esters of 2,4-D but do have the advantage of being less volatile (2).

Esters of 2,4-D are used primarily against broad-leaf plants that are relatively difficult to kill, as the esters have been found to be more phytotoxic to these plants than the inorganic and amine salts. The low molecular weight esters are relatively volatile, and for this reason must be used with caution around crops. High molecular weight esters have been formulated to reduce the volatility and eliminate this problem. The structure of the butyl ester of 2,4-D is shown below.

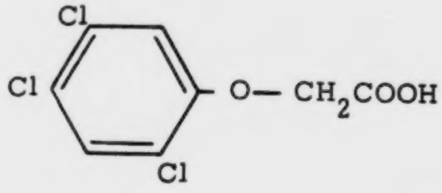


BUTYL ESTER OF 2,4-D (2)

Since all of the esters of 2,4-D are insoluble in water, formulation for agricultural use must be made with an organic solvent and a suitable emulsifier. Nonionic emulsifiers have been used most widely, although others are satisfactory (2).

2,4,5-T (2,4,5-Trichlorophenoxyacetic Acid)

This compound was first reported by Hammer and Tukey to be more effective than 2,4-D in killing woody plants. Chemically 2,4,5-T has the formula:



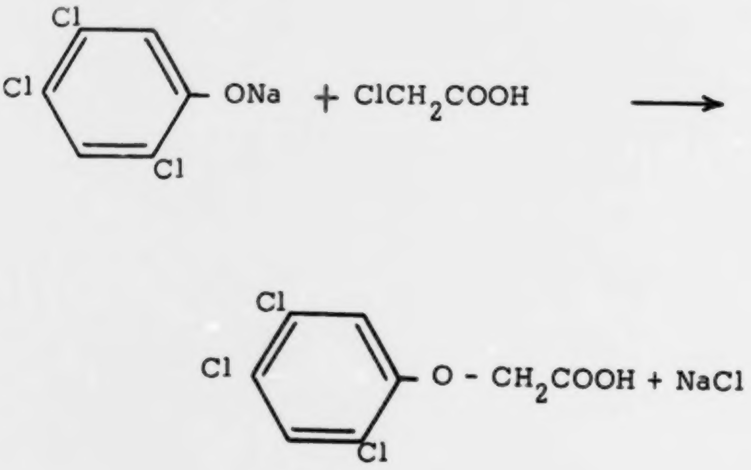
2,4,5-T

2,4,5-T is similar to 2,4-D in its chemical and physical properties. The acid is insoluble in water, it is a white solid with a melting point of 154-155°C. The esters, amine salts and sodium salts of 2,4,5-T resemble the corresponding derivatives of 2,4-D in solubility and other physical and chemical properties (2).

The amine salts of 2,4,5-T are difficult to prepare and therefore most of the commercial formulations of 2,4,5-T are esters. The esters are usually formulated using methyl, isopropyl, butyl and pentyl alcohols in the commercial products. The low-volatile esters, as is with 2,4-D, are used where sensitive cultivated crops are in adjacent areas (2).

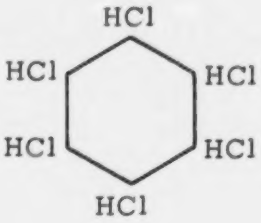
The esters of 2,4,5-T that are low molecular weight esters are less soluble in organic solvents than the corresponding 2,4-D compounds, but the higher esters such as propylene glycol butyl ether ester of 2,4,5-T are soluble in oil and aromatic solvents, while at the same time they exhibit polar properties that are valuable in promoting physiological action within plants (2).

2,4,5-T may be prepared by reacting 2,4,5 trichlorophenate with chloroacetic acid as shown below (2).



PREPARATION OF 2,4,5-T (2)

The BHC Series. The BHC series consists of compounds that are isomers of benzene hexachloride. BHC and lindane are the only compounds in the series which are widely used as insecticides. BHC - (1,2,3,4,5,6-Hexachlorocyclohexane) was discovered, or synthesized, by Michael Faraday in 1825 and in 1836 the structure of BHC was determined. Like DDT it was not until much later, 1902 in England, that the insecticidal value of BHC was discovered (2). In the early period of use the potency of BHC was so irregular that the isomers were separated and each subjected to insecticidal tests. The γ isomer was discovered to be highly toxic to the test insects but the α, β, and δ isomers exhibited relatively low toxicity. The γ isomer is known as lindane and mixtures that contain 99 percent of the γ isomer are known as lindane. BHC is formed by chlorinating benzene in the presence of light. The benzene accepts six atoms of chlorine forming a compound having the formula $C_6H_6Cl_6$. Theoretically several compounds having this formula are possible, however studies indicate that the main product of this reaction is 1,2,3,4,5,6 hexachlorocyclohexane, having one chlorine and one hydrogen atom attached to each carbon in the cyclohexane ring (2). Hassel and Bijvoet list the possible isomers of BHC as thirteen (2). The isomers of BHC are stable in the presence of strong aicds, heat, air, CO_2, and light. The alpha, gamma, delta, and epsilon isomers are dehydrohalogenated in the presence of alkalies and form 1,2,4-



BHC

trichlorobenzene as the major product with small amounts of 1,2,3, and 1,3,5-trichlorobenzenes formed. In the presence of alkali at elevated room temperature the beta isomer is also readily broken down (2).

$$C_6H_6Cl_6 + 3OH^- \longrightarrow C_6H_3Cl_3 + 3H_2O + 3Cl^-$$

DECOMPOSITION OF BETA ISOMER OF BHC (2)

Rainwater and Ivy (2) found that when powdered limestone was mixed with BHC it did not cause decomposition, but that calcium arsenates caused decomposition of commercial BHC and the pure gamma isomer when mixed together (2). With the delta isomer present the dehydrochlorination of the gamma isomer was prevented when mixed with calcium arsenate.

Lindane - the name lindane refers to preparations that contain at least 99 percent of the gamma isomer of BHC. Lindane has been used widely as an insecticide because it is relatively free from the odor characteristic of commercial BHC. Lindane is prepared by fractional crystallization from selective solvents and is formulated as solutions, aerosols, wettable powders and emulsifiable concentrates (2).

Lindane is volatile at temperatures above room temperature and sublimes readily. Because of this lindane was used widely in evaporators in the control of houseflies until the housefly developed a tolerance to it.

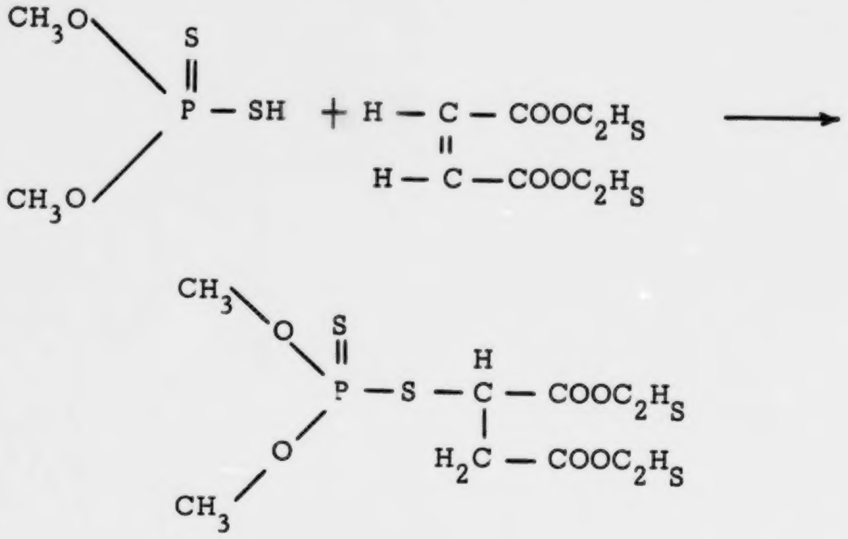
Organic Phosphates

The organic phosphorus pesticides are characterized by similar chemical structure as they may all be considered as derivatives of phosphoric acid and by similar mode of action. Some of these compounds are parathion, methyl parathion, malathion, EPN, systox, TEPP and phosdrin.

Malathion (0,0-dimethyl S-(1,2-dicarboethoxyethyl) dithiophosphate)

Malathion was first made available in December, 1950, by the American Cyanamid Company, who claimed it to be less toxic to mice and rats than parathion, although almost equal to parathion in insecticidal activity. It is estimated that malathion is about 100 times less toxic to warm blooded animals than parathion and about two to four times less toxic to insects.

Malathion is prepared by the reaction shown on the following page (3). The technical grade of malathion is 85 to 95 percent pure, has a boiling point of 155-157°C, and the vapor pressure is reported



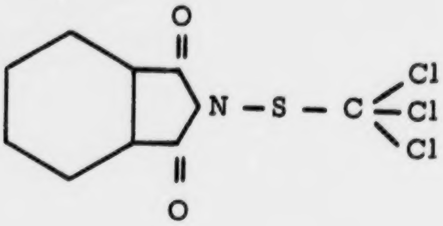
PREPARATION OF MALATHION (3)

to be 4 x 10^{-5} mm Hg at 30°C. It is liquid at room temperature and yellow to dark brown in color (1). Malathion crystallizes at low temperatures, the melting point being -7°C (2). The liquid has a specific gravity of 1.23 at 25°C and a solubility in water of approximately 150 mg/l. It is miscible with many organic solvents including alcohols, esters, ketones, ethers, aromatics and alkylated aromatic hydrocarbons and vegetable oils. It has limited solubility in petroleum oils. It is reported that liquid malathion is stable between a pH of 5 and 7 but it will hydrolyze under alkaline conditions (1). Malathion at a pH of 12 was hydrolyzed almost instantaneous, at pH 9 50 percent was hydrolyzed in about 12 hours and as reported no hydrolysis occurred at pH 5-7 in 12 days (6). The laboratory experiments did not agree with the reported hydrolysis of malathion. At a pH of 7 experiments indicated that malathion was 32 percent hydrolyzed in 10 days. Tests conducted to study the effect of pH in the range of 4 to 8 on hydroylsis indicated the least hydrolysis occurred at a pH of 6. Pure malathion is fairly odorless; however the technical grade has a strong garlic odor. Although malathion emulsions that are formed with nonionic materials may be expected to have a long "shelf life," certain of the anionic emulsifiers may not be as satisfactory. In general a slightly acidic or neutral reaction with pH 4-7 and a low moisture content are desirable characteristics for the inert materials used in the preparation of malathion wettable powders (6). Some of the carriers giving the most stable formulations include acidic frianites, acidic kaolin, and diatomaceous earths.

Organic Fungicides

Captan (N-(Trichloromethylthio)-1,2,3,6-tetrahydrophthalimide)

Captan has been known by several names, such as Orthocide 406, S.R. 406, and is patented under U. S. Patent 2,553,770 for its fungicidal properties. It is made by reacting tetrahydrophthalic anhydride with ammonia to form an imide, which is then condensed with perchloro-methyl mercaptan to form captan (2).



CAPTAN (2)

The pure compound is in the form of white crystals and has a melting point of 172°C. The technical grade is a yellow amorphous powder that has a pungent odor, and a melting point of 158-164°C. It has a density of 1.5 and is nearly insoluble in water and petroleum oils, and partially soluble in acetone, benzene and toluene. It is incompatible with lime and other alkaline materials, although it is compatible with most other pesticides (5).

Captan is used as a general fungicide for fruit trees, flowers and vegetables. It can be absorbed through the skin when sealed from the atmosphere but is not absorbed on skin exposed to air (5).

CHAPTER II

PREPARATION OF STOCK MIXTURES OF PESTICIDES

In a review of the literature that has been published concerning the solubility of pesticides in water there is a considerable variation in the reported data. Several sources have indicated that some of the chlorinated hydrocarbon pesticides are soluble to a degree, while others indicate that these same pesticides are essentially insoluble in water.

The techniques and methods which were used to prepare the stock mixtures of radioactive and inert pesticides in these studies are discussed in this chapter.

Preparation of Aldrin, BHC, Captan, Dieldrin, DDT, and 2,4,5-T

Each misture was prepared by placing a specific amount of radioactive pesticide into 18 liters of distilled water. The aldrin mixture consisted of 0.36 mg of radioactive aldrin in 18 liters of distilled water which resulted in a concentration of 0.02 mg/l with a initial count of 700 c/min/ml. The dieldrin mixture contained 0.90 mg of radioactive dieldrin in 18 liters of distilled water which resulted in a concentration of 0.05 mg/l with an initial count of 1270 c/min/ml. The DDT mixture consisted of 0.1883 mg of radioactive DDT in 18 liters of distilled water which resulted in a concentration of 0.0105 mg/l with an initial count of 790 c/min/ml. The BHC mixture consisted of 0.32 mg of radioactive BHC in 18 liters of distilled water which resulted in a concentration of .0178 mg/l with an initial count of 2,000 c/min/ml. The captan mixture consisted of 10.0 mg of radioactive captan in 18 liters of distilled water which resulted in a concentration of 0.556 mg/l with an initial count of .410 c/min/ml. The 2,4,5-T mixture consisted of 0.155 mg of radioactive 2,4,5-T in 18 liters of distilled water which resulted in a concentration of 0.0086 mg/l with an initial count of 1,100 c/min/ml.

Each of the mixtures of pesticides was agitated with a mechanical stirrer for an extended period of time, then filtered through a 450 mμ membrane filter to remove large particles or aggregates of pesticide. Each filtrate was used in the investigations as the original mixture and the count of each mixture was observed before each test. The original count remained constant throughout all tests and the mixture was considered as being uniform.

The amount of pesticide in the mixture before and after tests was determined by utilizing a Packard Tri-Carb Liquid Scintillation Spectrometer. For any given solution, five milliliter samples were placed into three bottles to obtain a triplicate check.

Fifteen milliliters of scintillation liquid was added to each bottle and the samples were counted for ten minutes. To determine the background count of the counter, samples were counted that contained five milliliters of distilled water and fifteen milliliters of scintillation liquid. The background count was subtracted from each sample count. The concentration of pesticide in a given mixture was calculated by relating the quenching factor of the solution, the count of the mixture and the specific activity of the radioactive pesticide used

Preparation of 2,4-D

Stock solutions of 2,4-D in water were prepared by mixing 19 liters of distilled water with 1872 mg. of inert 2,4-D and 28 mg. of radioactive 2,4-D. This produced a mixture containing a concentration of 100 mg/l 2,4-D. The radioactive portion of the 2,4-D was used to measure the residual amount in solution following a given test. Due to the radioactive portion of 2,4-D, the stock solution had an initial count of about 8300 counts per minute per milliliter of solution.

The stock solution was prepared by mixing the 2,4-D and distilled water with an electric stirrer in a five-gallon pyrex container for about two days. At this time the mixture was checked by two methods to determine if the 2,4-D was in solution. It was first sampled and then allowed to settle for two days before being sampled again at different depths in the container. The sample showed no difference in concentration. A second method of determining whether or not the 2,4-D mixture was in solution was to filter 250 milliliters of the mixture through a 450 mμ millipore filter. The filtrate showed no difference in concentration of 2,4-D as compared with the original stock solution. Since neither of these two methods of sampling showed any change in the concentration, it was concluded that the mixture was in solution.

The amount of 2,4-D remaining in solution, following a given test, was determined by measuring the residual radioactive 2,4-D that had been added as a tracer. Triplicate, one-milliliter samples were used throughout these investigations and the samples were counted in an internal proportional gas flow counter using a 90 percent argon and 10 percent methane gas mixture. The samples were counted for either two or three minutes depending on the counting rate. A background count was obtained by five or ten minute counts and subtracted from the actual count to obtain the true count of the sample. The residual concentration of 2,4-D was then calculated from the count of the sample.

Preparation of Malathion

The stock solutions of malathion used in the carbon adsorption test were prepared by mixing a calculated amount of ninety-five percent pure malathion, obtained from the American Cyanamid Company, with a specified amount of distilled water. The solutions were prepared one hour before each was to be used to eliminate the effects of hydrolysis. The solutions were mixed with an electric mixer for one half hour prior to conducting the experiments to ensure that the malathion was in solution.

The amount of malathion remaining in solution following the carbon adsorption tests was determined with a Barber-Colman Series 5000 Gas Chromatograph equipped with an electron-capture detector, following extraction of the residual malathion with hexane.

In the balance of the tests conducted with malathion a stock solution was prepared by mixing eight liters of Lexington tap water and 3 ml of ninety-five percent pure malathion in a ten liter Pyrex bottle. These proportions left some undissolved malathion in the bottom of the bottle, thereby maintaining the concentration of malathion in the solution in the range of 100 to 180 mg/l. The bottles were sealed until used. The samples used in each test were drawn off in one container and then stirred to ensure equal concentration of malathion in all samples.

In all of the investigations undertaken (with the exception of the carbon adsorption tests), the amount of malathion in solution was measured colorimetrically (46,47,48). Malathion is decomposed by alkali in ethanol to sodium 0,0-dimethyl dithiophosphate and sodium fumarate. The sodium 0,0-dimethyl dithiophosphate is then converted to a cupric complex which is soluble in CCl_4 with the formation of an intense yellow color. The color intensity is proportional to the concentration of 0,0-dimethyl dithiophosphoric acid and is measured colorimetrically at 420 mμ, the absorption peak. The corresponding amount of insecticide is determined by comparison with standards prepared with known amounts of pure insecticide. The standard curve used in these investigations is shown in Figure 2-1.

Testing of Stock Mixtures of Pesticides

Due to the variation reported in the literature concerning the solubility of pesticides in water, tests were initiated to determine if the mixtures used in these studies were in solution or if, in reality, the solutions were actually suspensions of pesticides in water. Tests were conducted by sampling the pesticide mixtures in the storage containers (20 liter Pyrex) that had been setting undistrubed for a minimum period of one month. Samples were withdrawn from the top and bottom of the liquid with a minimum of agitation. Concentrations of the samples indicated that the stock mixture of aldrin, dieldrin, and DDT had settled to a significant degree, in fact some concentrations from the bottom of the containers

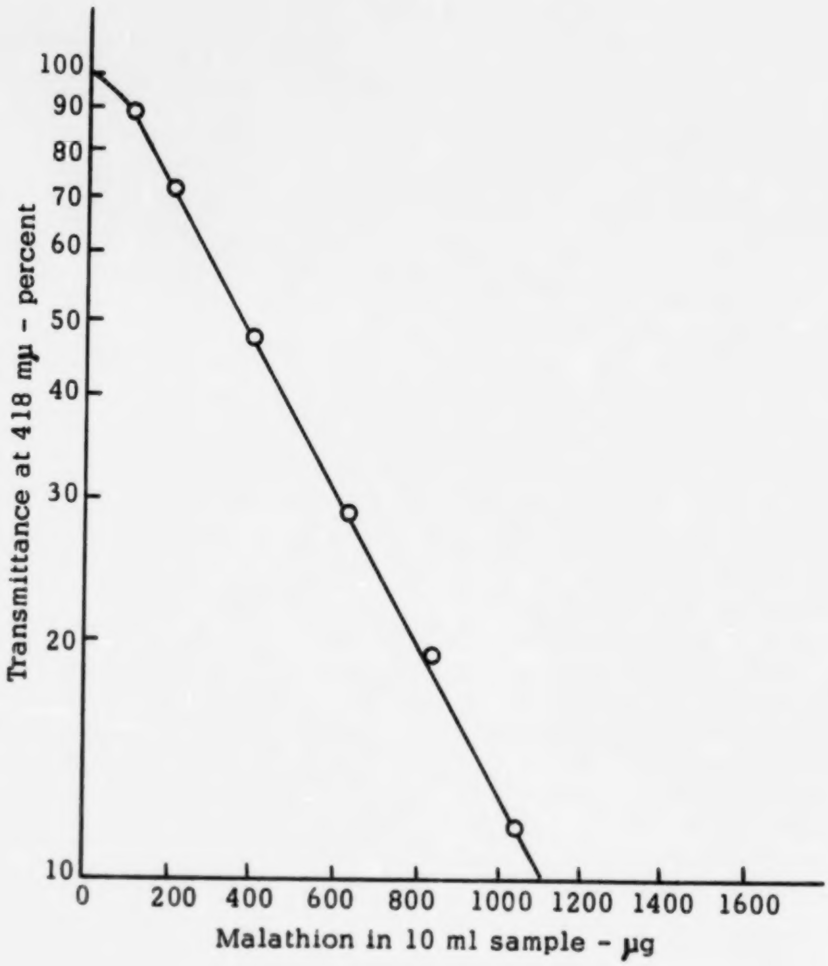


Figure 2-1

STANDARD CURVE FOR
MALATHION DETERMINATION PROCEDURE

were as much as double that from the top. Similar samples withdrawn from the storage containers holding captan, 2,4,5-T, BHC, and 2,4-D showed no significant difference in concentration, indicating that the compounds were probably in true solution at that concentration.

Table 2-1 lists the radioactive pesticides used in these studies, with their chemical names and specific activities.

TABLE 2-1

PROPERTIES OF RADIOACTIVE PESTICIDES USED

Pesticide	Chemical Name	Specific Activity DPM	Specific Activity CPM*
Aldrin	Hexachorohexahydro-endo, exo-dimethano-naphtalene	54.39×10^6	25.18×10^6
Dieldrin	Hexachoroepoxyoctahydro-endo, exo-dimethano-naphthalene	54.83×10^6	25.39×10^6
DDT	Dichlorodiphenyltrichloroethane	162.95×10^6	75.46×10^6
2,4-D	2,4-Dichlorophenoxyacetic Acid	191.80×10^6	88.80×10^6
BHC	1,2,3,4,5,6-Hexachlorocyclohexane	244.20×10^6	113.06×10^6
Captan	N-(Trichloromethylthio)-1,2,3,6-tetrahydrophthalimide	1.56×10^6	0.72×10^6

*For Packard Tri-Carb Liquid Scintillation Spectrometer, with a water sample. The counting efficiency of the counter combined with the quenching effect of a water sample was calculated to be 46.3 percent.

CHAPTER III

VOLATILITY OF PESTICIDES

The objective of this phase of the project was to determine if certain pesticides that were being studied were volatile. The volatility of these pesticides was evaluated under two conditions; first, the pesticides in solid form were studied and second, a mixture of the pesticide and water was aerated and the volatility under these conditions studied.

To study the effect of temperatures at and above room temperature on the volatility of pesticides in solid form the following procedure was followed. Small aluminum weighing dishes were brought to a constant weight and a known amount of each of the pesticides being investigated was spread over the bottom of the dishes. Three dishes were prepared in the above manner for each pesticide and one of each placed in constant temperature rooms at 20°C, 30°C, and 40°C. The samples were weighed periodically and the loss in weight of each sample was recorded throughout the one hundred day test period. During the first few days of the test several of the samples showed a higher rate of loss than is indicated by the curves (Figure 3-1 through 3-8). This initial loss was assumed to be due to impurities or moisture in the sample, and the constant

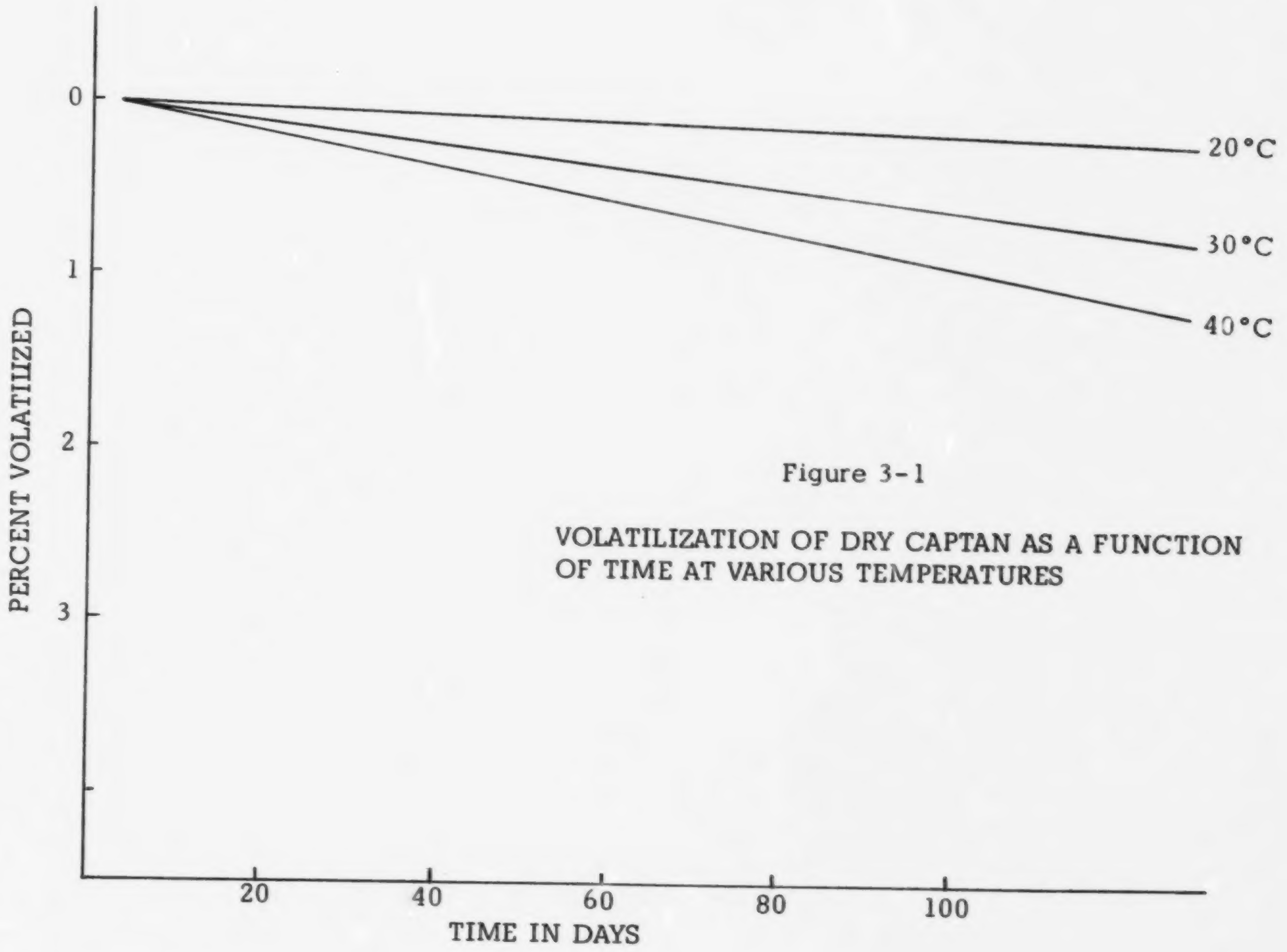


Figure 3-1

VOLATILIZATION OF DRY CAPTAN AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES

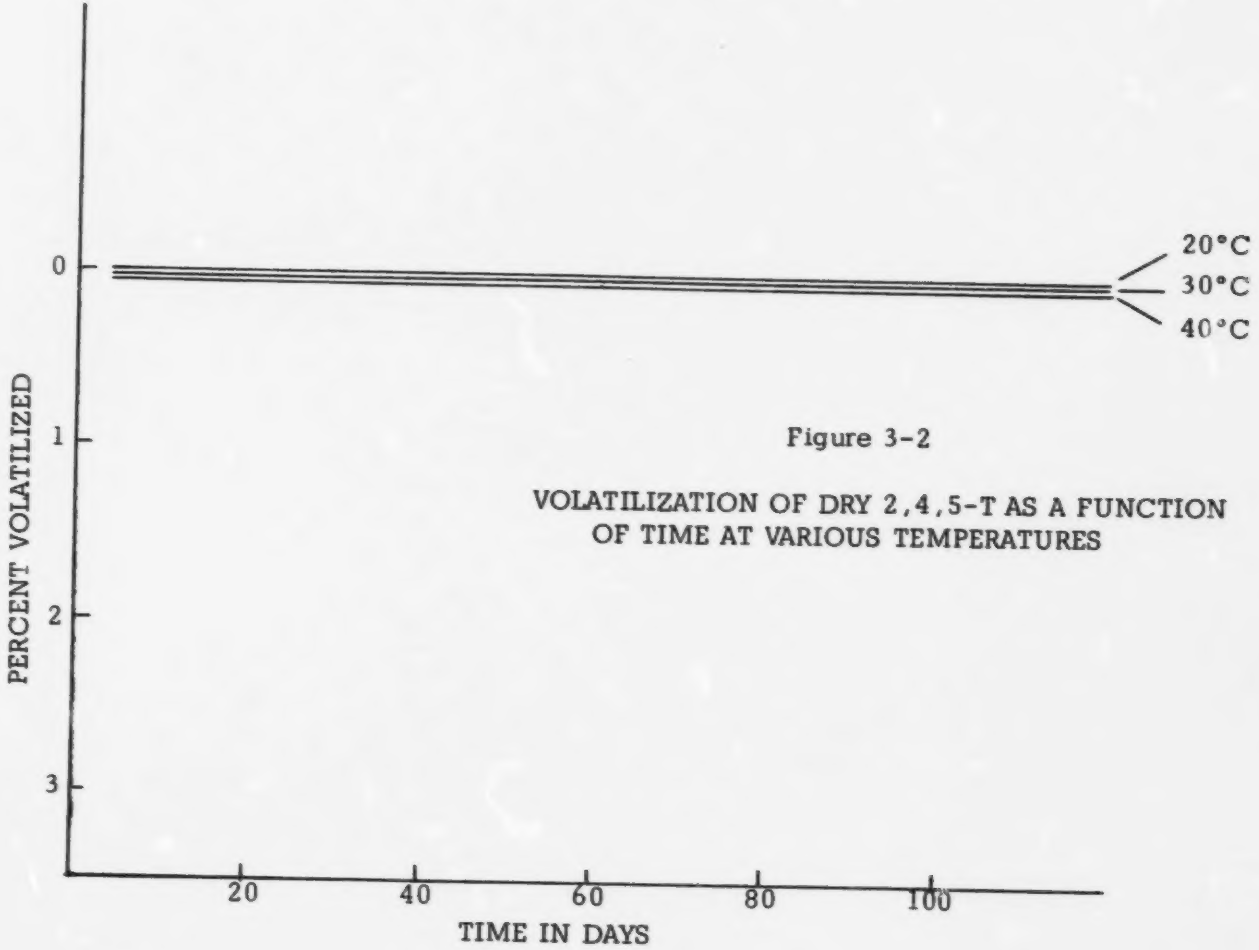


Figure 3-2

VOLATILIZATION OF DRY 2,4,5-T AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES

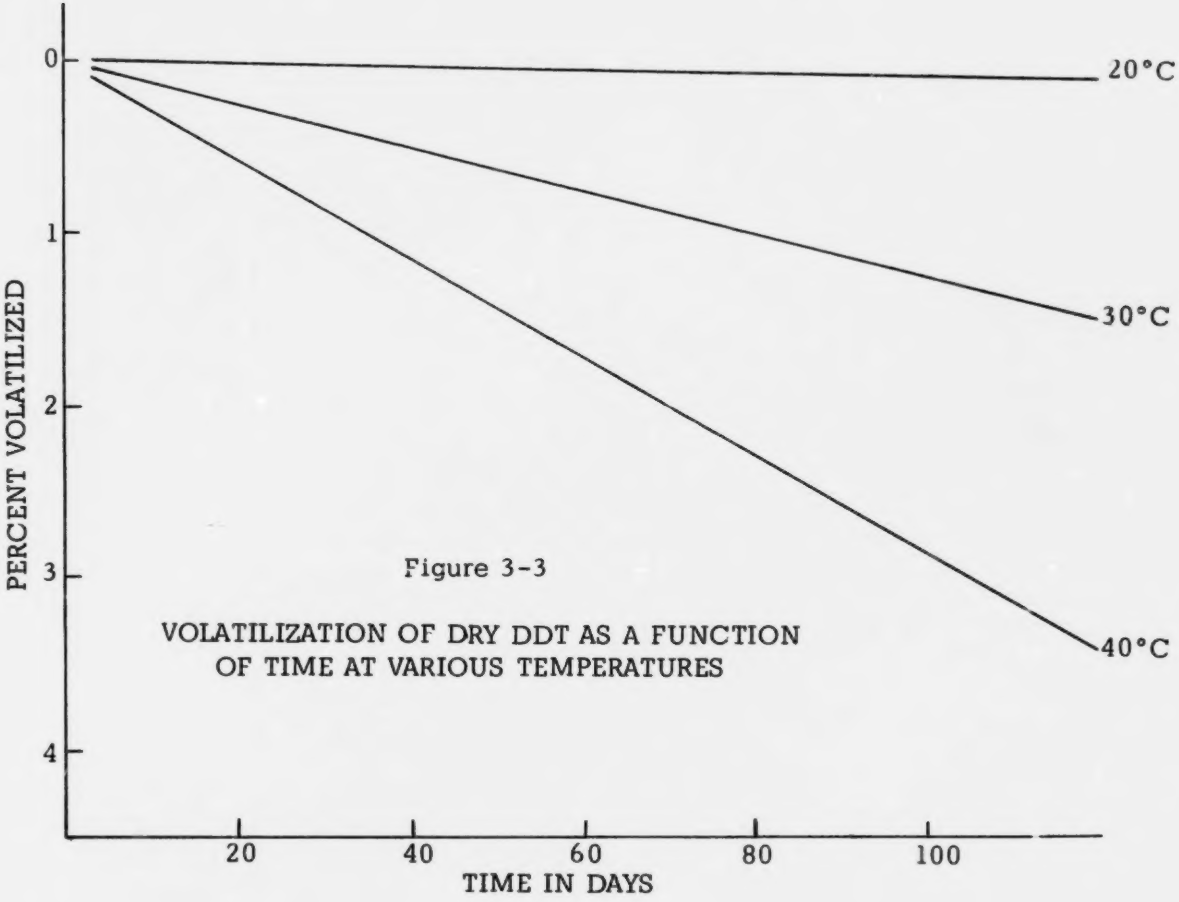


Figure 3-3

VOLATILIZATION OF DRY DDT AS A FUNCTION
OF TIME AT VARIOUS TEMPERATURES

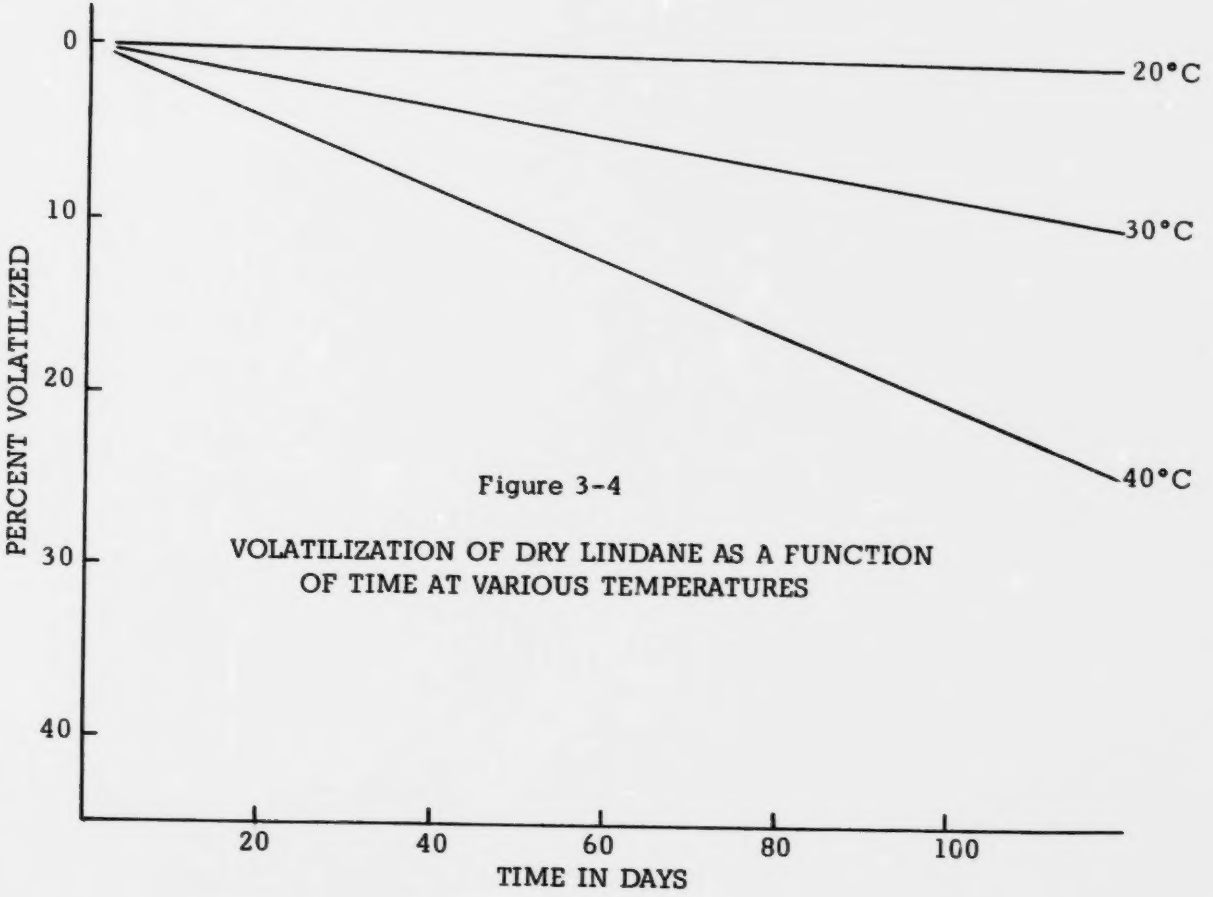


Figure 3-4

VOLATILIZATION OF DRY LINDANE AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES

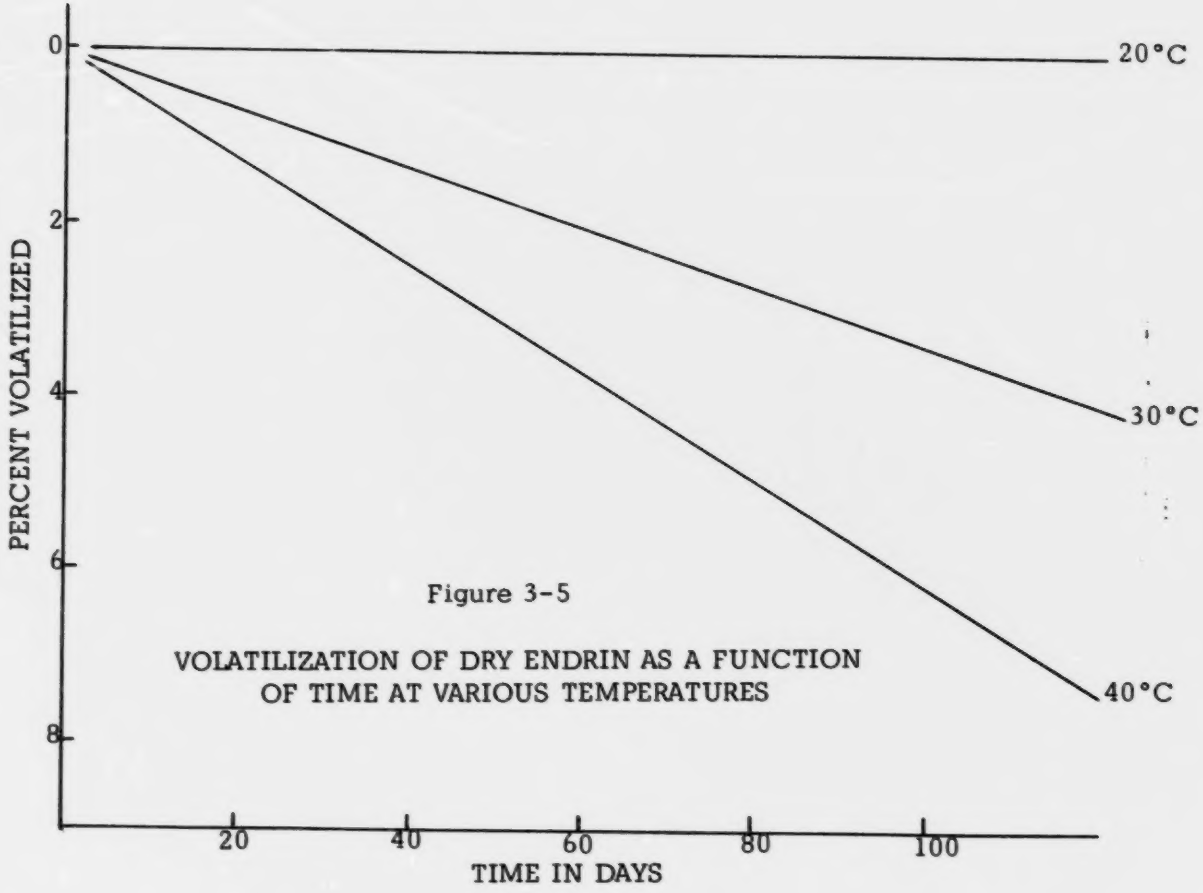


Figure 3-5

VOLATILIZATION OF DRY ENDRIN AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES

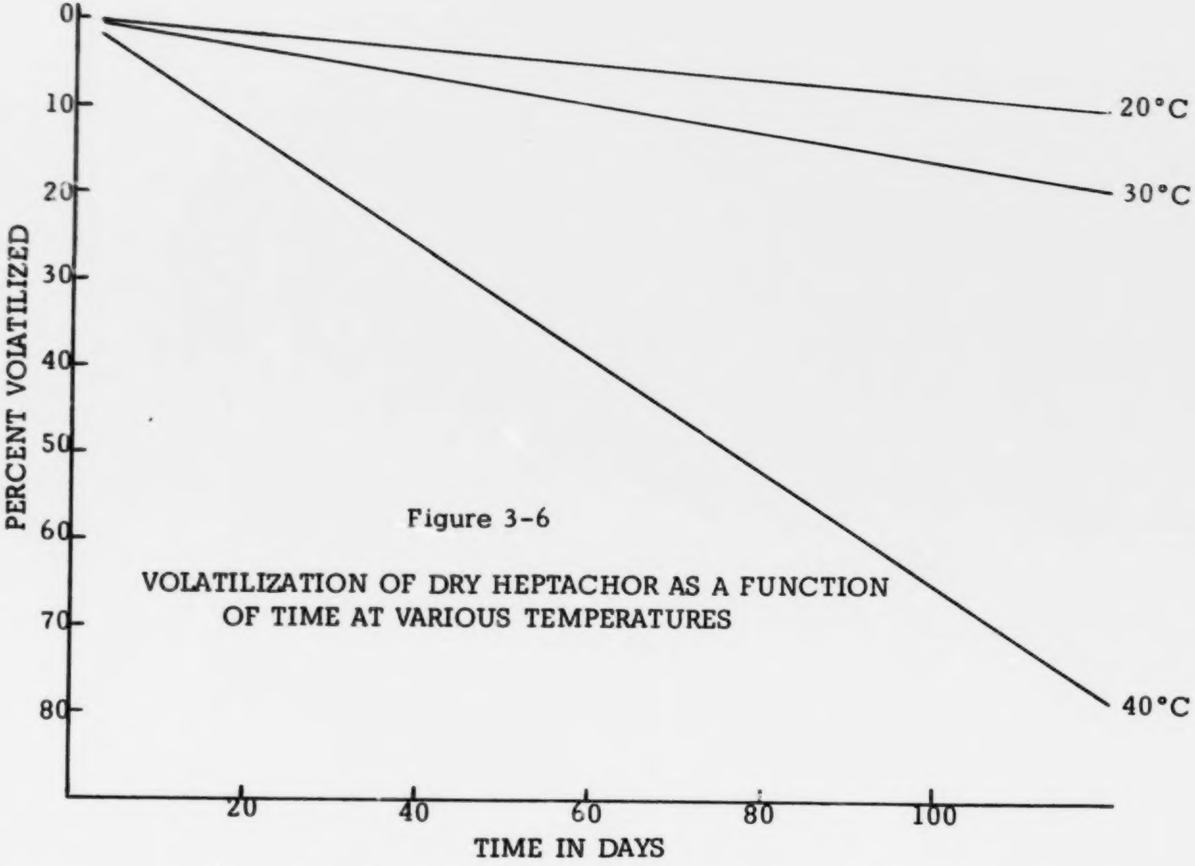


Figure 3-6

VOLATILIZATION OF DRY HEPTACHOR AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES

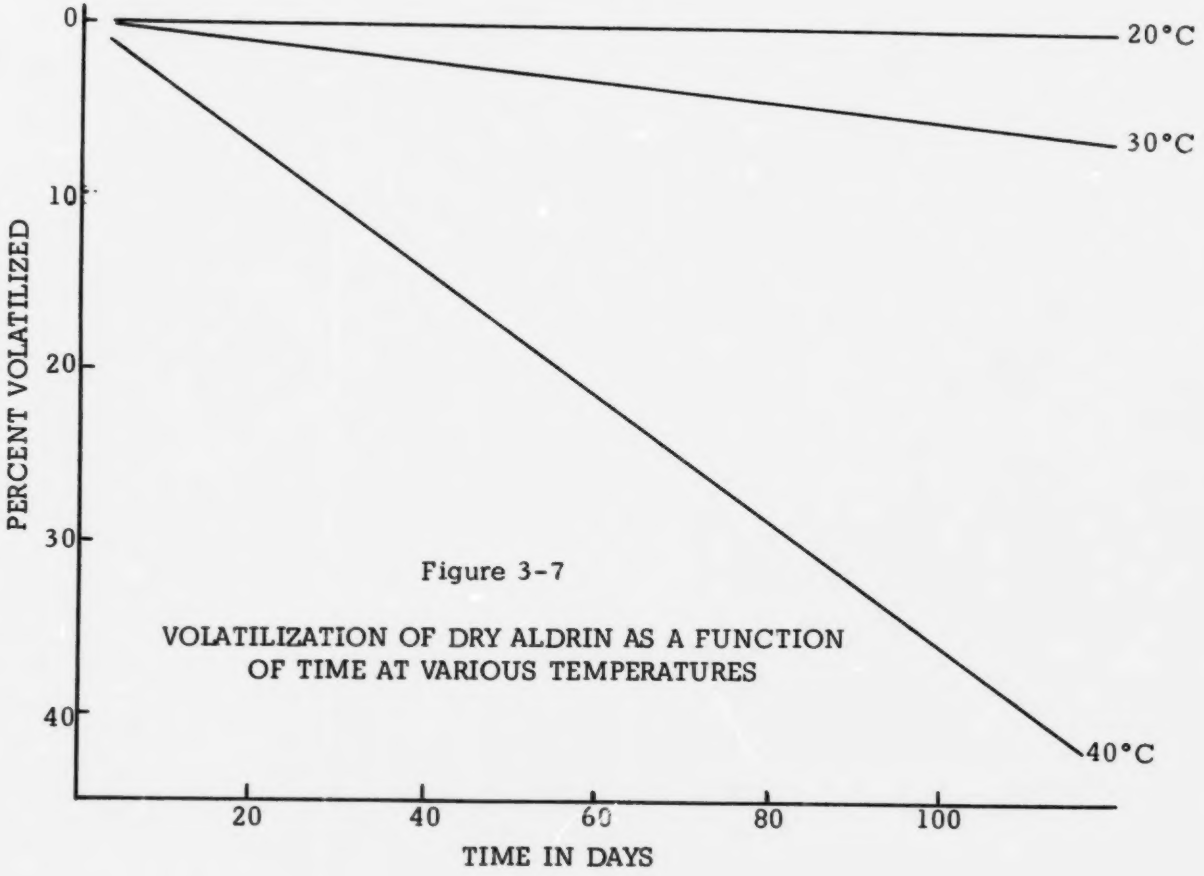


Figure 3-7

VOLATILIZATION OF DRY ALDRIN AS A FUNCTION
OF TIME AT VARIOUS TEMPERATURES

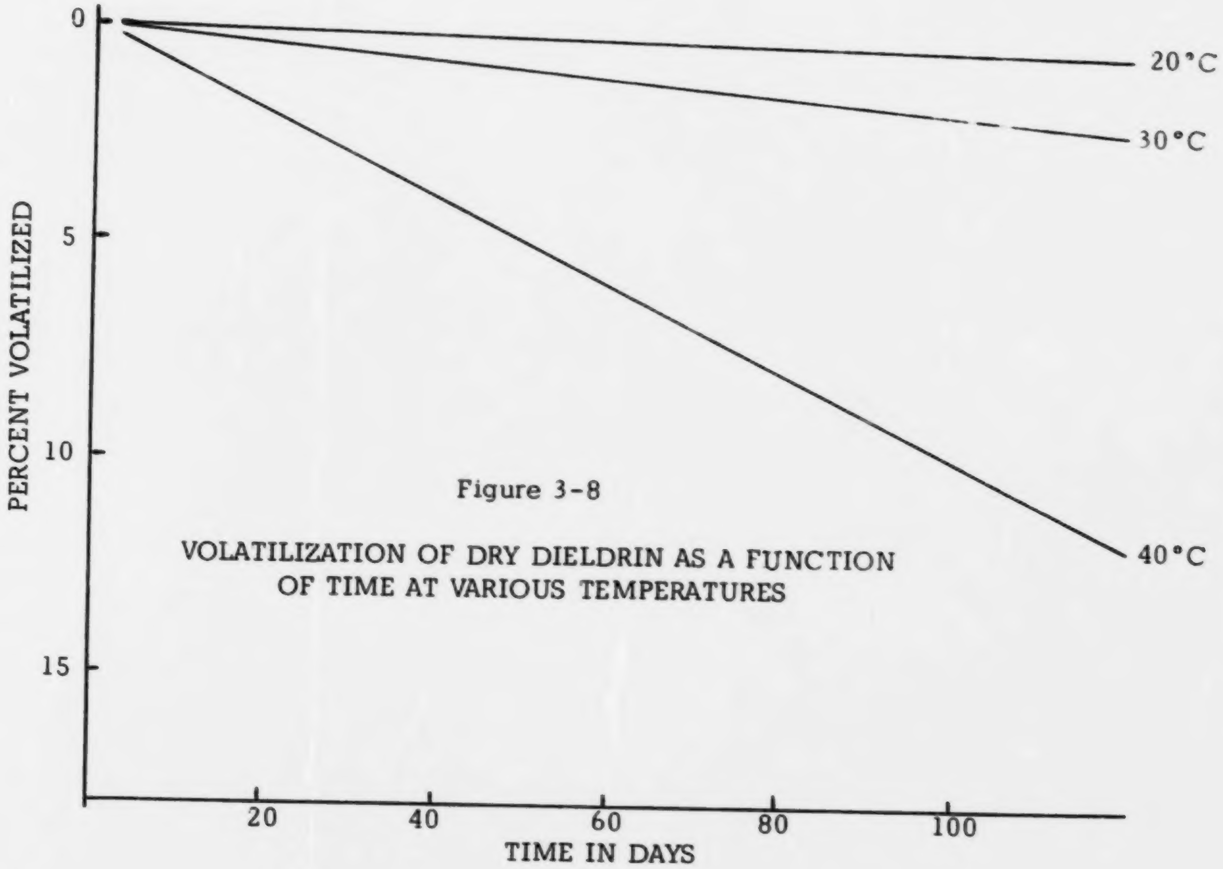


Figure 3-8

VOLATILIZATION OF DRY DIELDRIN AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES rate of loss that appeared over the entire test period is shown on the curves.

In the second phase of this experiment stock mixtures of radioactive pesticides and water were aerated at different temperatures to determine if aeration would decrease the concentration of the pesticide in the samples. The experiments were carried out in the following manner. Glass cylinders 7.5 cm in diameter with a capacity of 2,000 ml were used to contain the 1500 ml sample of stock mixture. Air was supplied to each cylinder through an air supply header, and the airflow was measured by a flow meter placed in the line between the air supply and the header. The air was introduced into the liquid at the bottom of the cylinder through a diffuser stone to provide agitation and a maximum air surface exposure. The air flow to each cylinder was regulated to supply 90 ml of air per minute. Triplicate samples were obtained from each cylinder before aerating and collected periodically during the test period. Tests were conducted at temperatures of 10°C, 20°C, 30°C, and 40°C. The volume of water that evaporated during the test was replaced with distilled water and allowed to agitate before each periodic sampling. In preliminary tests conducted over a wide range of flow rates, 0 to 2000 ml per minute, it was determined that flows from 25 to 2,000 ml per minute did not affect the rate or the amount of removal of the pesticides from water.

Figures 3-9 through 3-16 show the percent loss in concentration as a function of time of aeration at different temperatures. The greatest effect due to temperature on the removal was that as the temperature was increased the samples in general reached a maximum removal in a shorter time than at lower temperatures. For example in Figure 3-9 aldrin at 10°C reached a maximum removal in 70 to 80 hours while at 40°C a maximum removal was reached in 35 to 40 hours (Figure 3-15). This fact was also illustrated in the tests with BHC, Figure 3-10 and Figure 3-16 in which the time of maximum removal varies from ± 120 hours to ± 60 hours respectively.

Figure 3-17 shows the maximum percent removal by aeration as a function of temperature. This curve illustrates that, in general, temperature does not affect the maximum removal, but only the rate at which the removal is achieved.

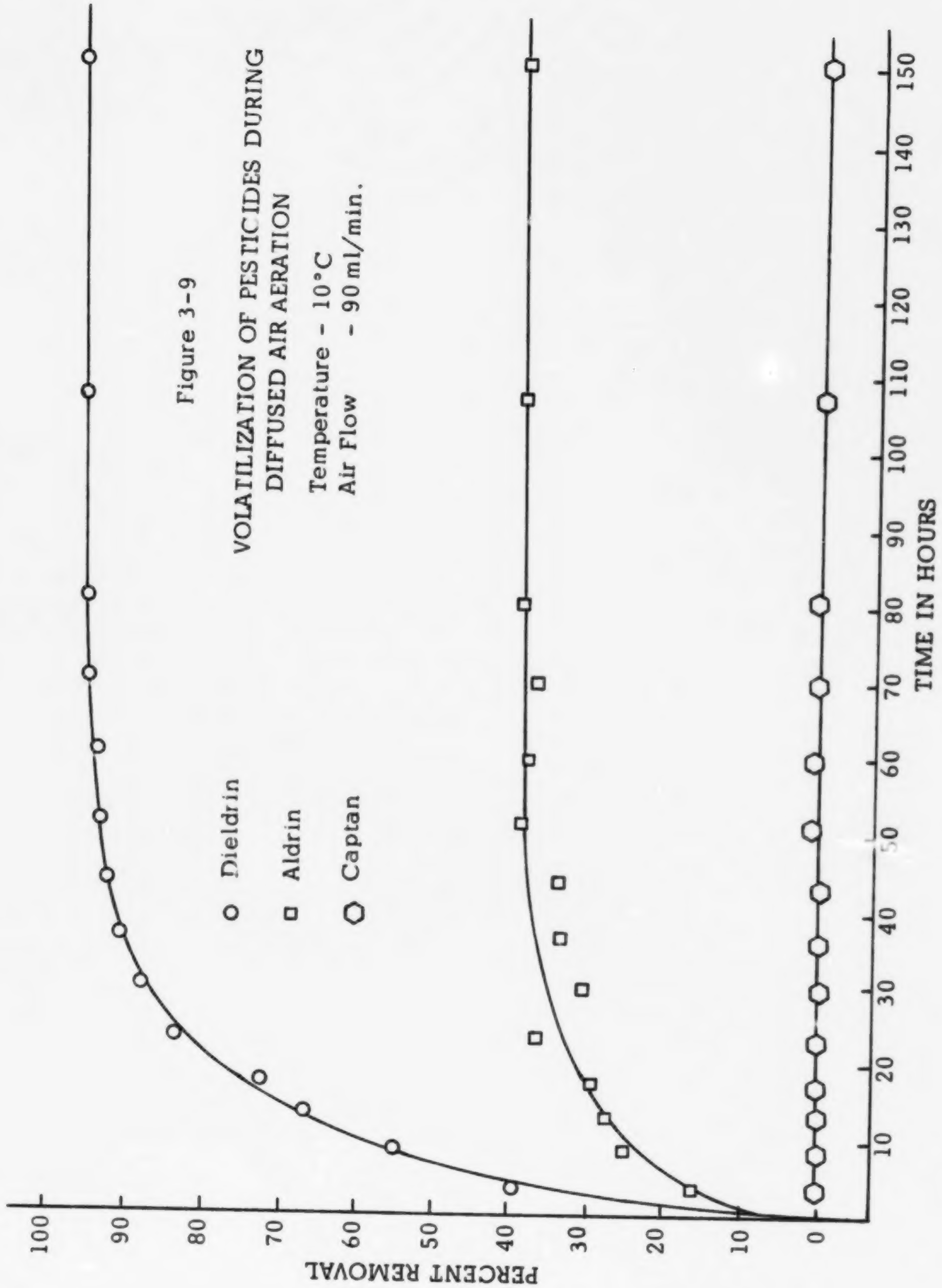


Figure 3-9

VOLATILIZATION OF PESTICIDES DURING DIFFUSED AIR AERATION

Temperature - 10°C
Air Flow - 90 ml/min.

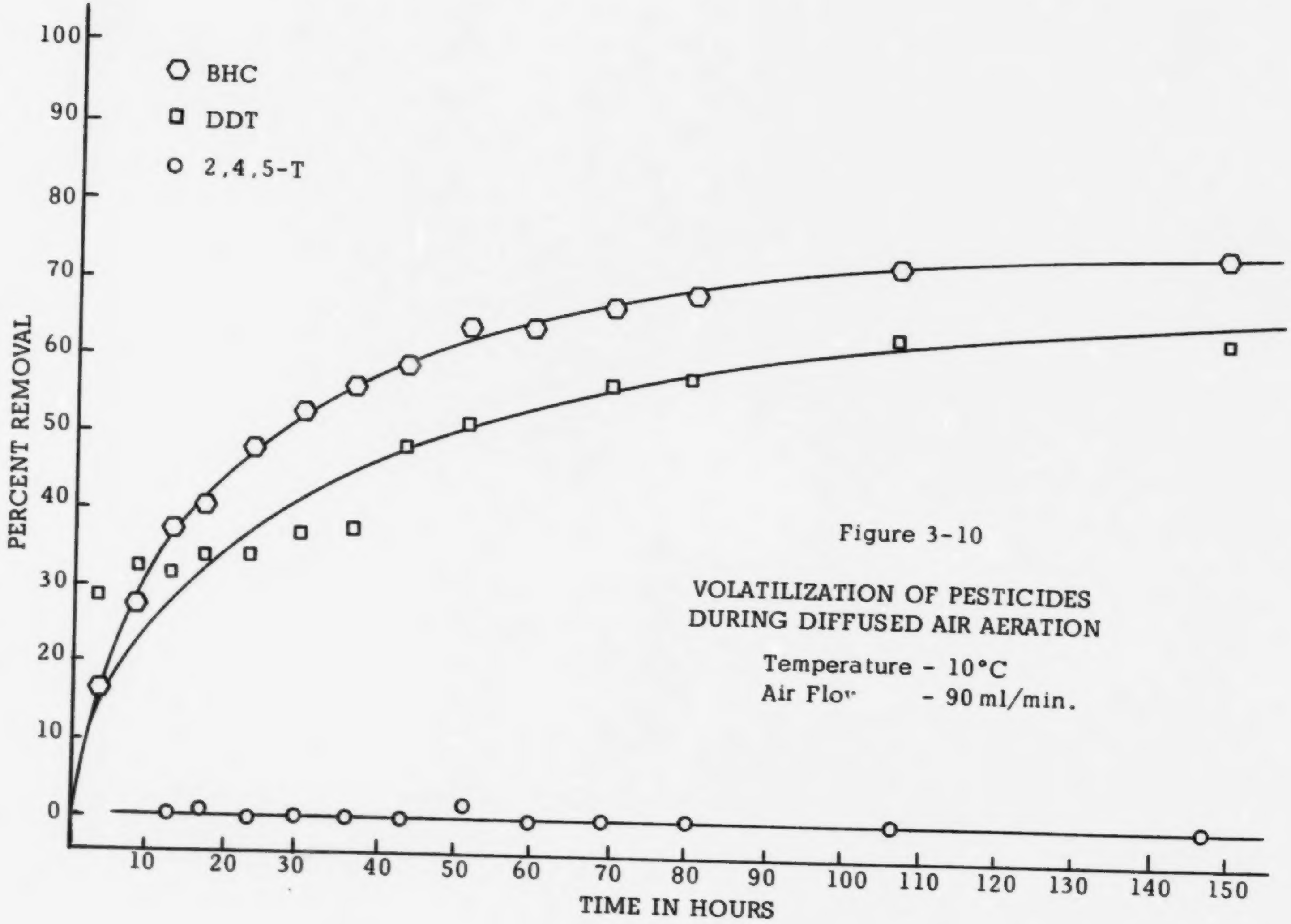


Figure 3-10

VOLATILIZATION OF PESTICIDES DURING DIFFUSED AIR AERATION

Temperature - 10°C
Air Flo' - 90 ml/min.

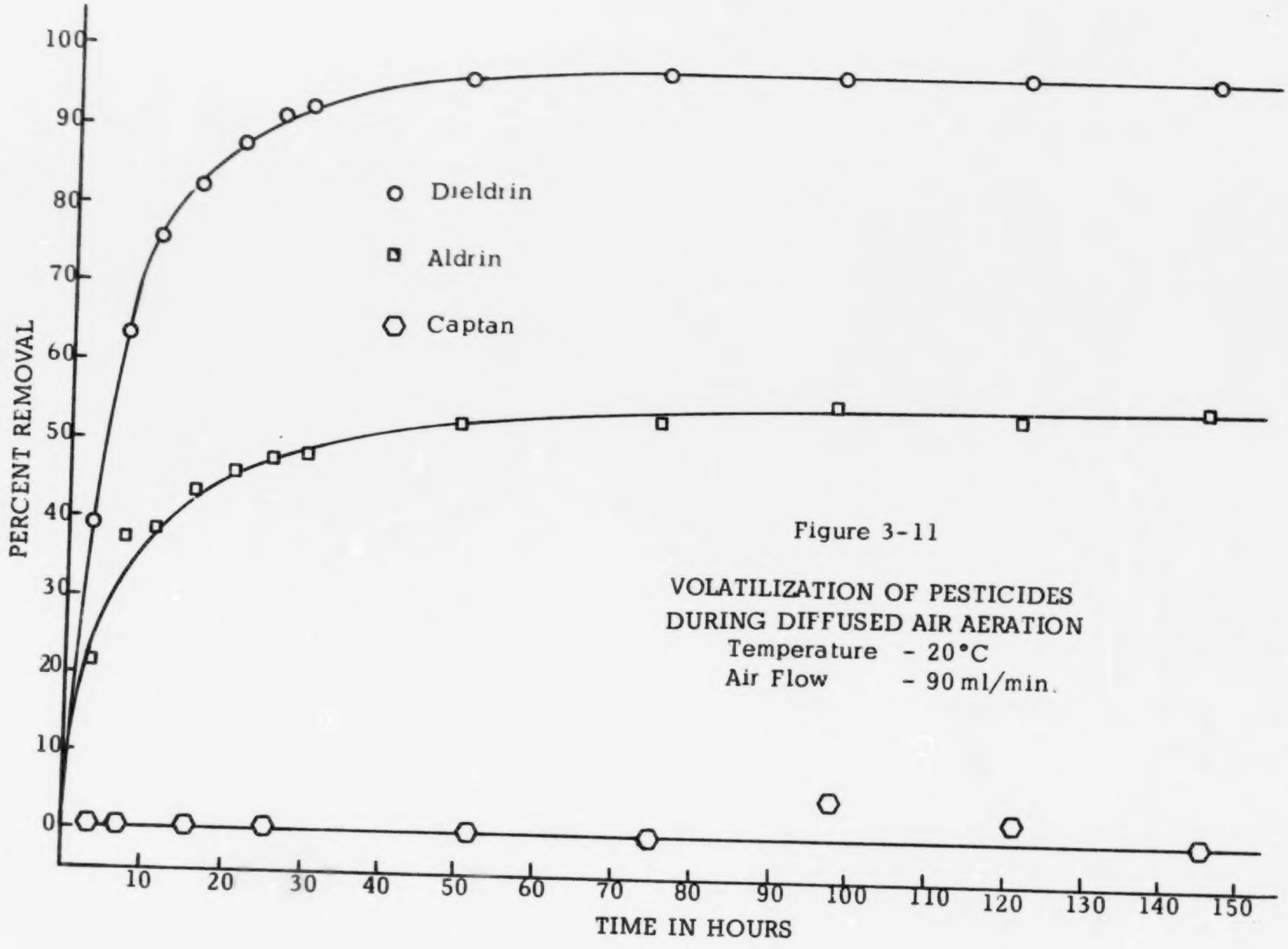


Figure 3-11

VOLATILIZATION OF PESTICIDES
DURING DIFFUSED AIR AERATION
Temperature - 20°C
Air Flow - 90 ml/min.

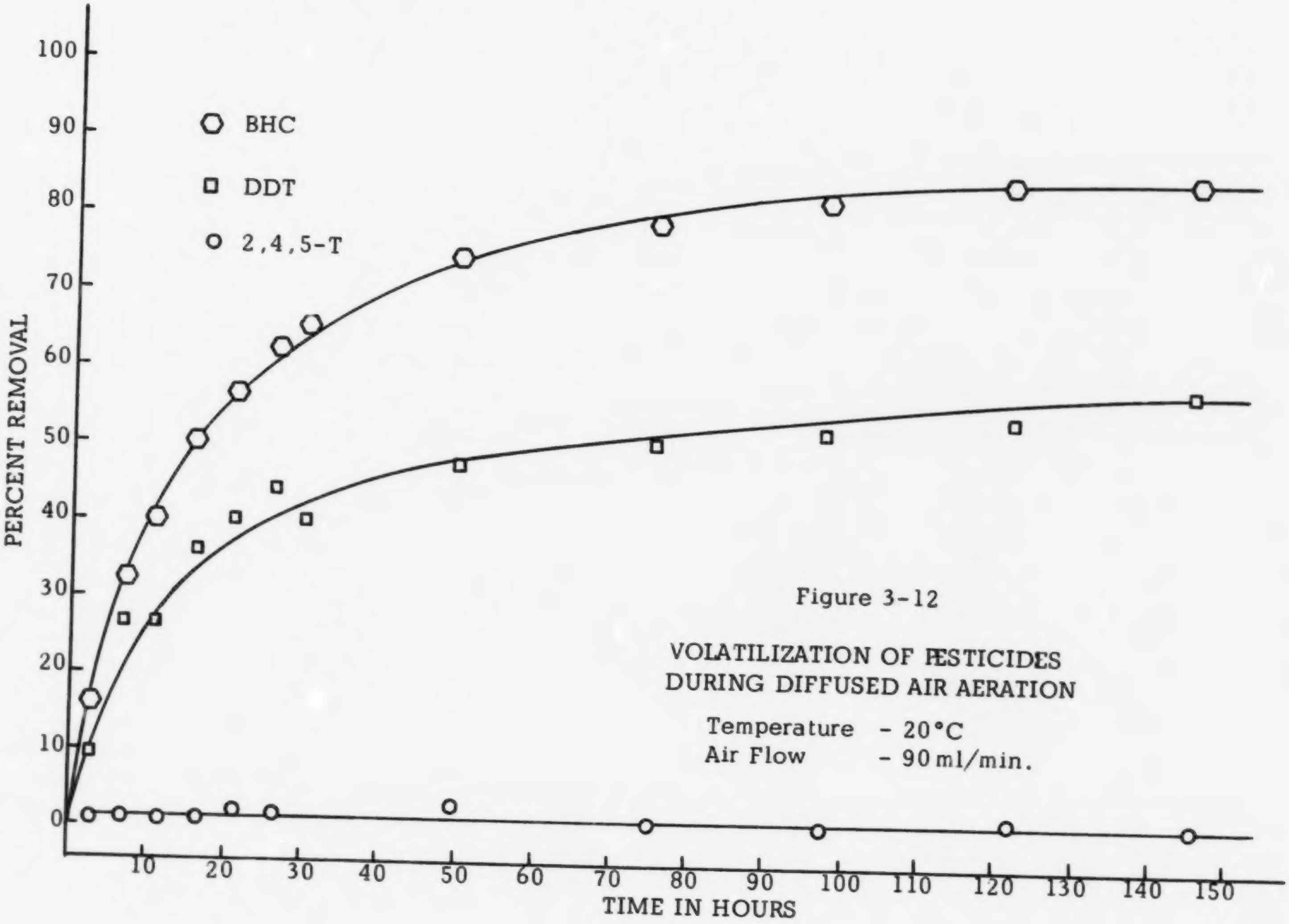


Figure 3-12

VOLATILIZATION OF PESTICIDES DURING DIFFUSED AIR AERATION

Temperature - 20°C
Air Flow - 90 ml/min.

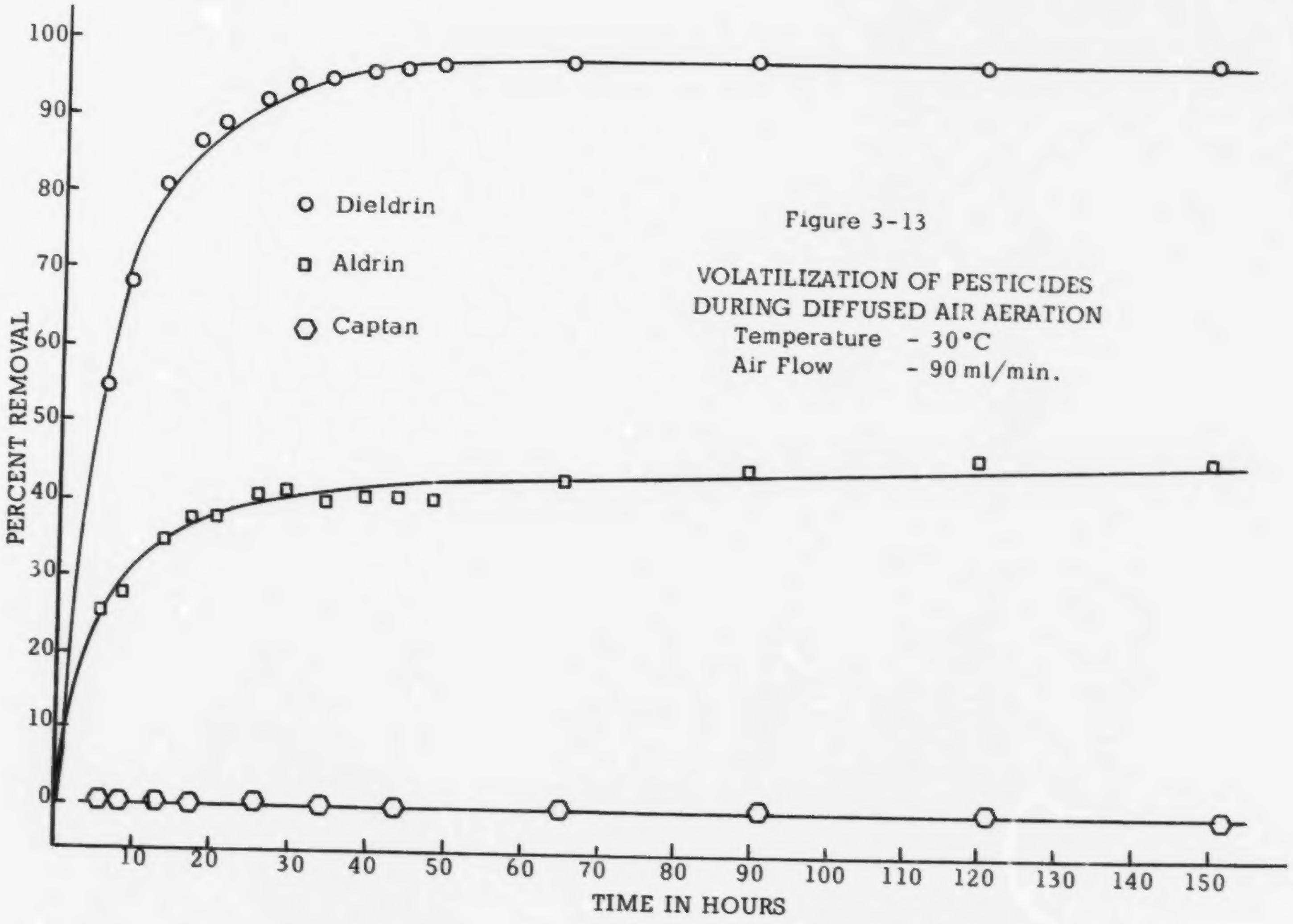


Figure 3-13

VOLATILIZATION OF PESTICIDES
DURING DIFFUSED AIR AERATION
Temperature - 30°C
Air Flow - 90 ml/min.

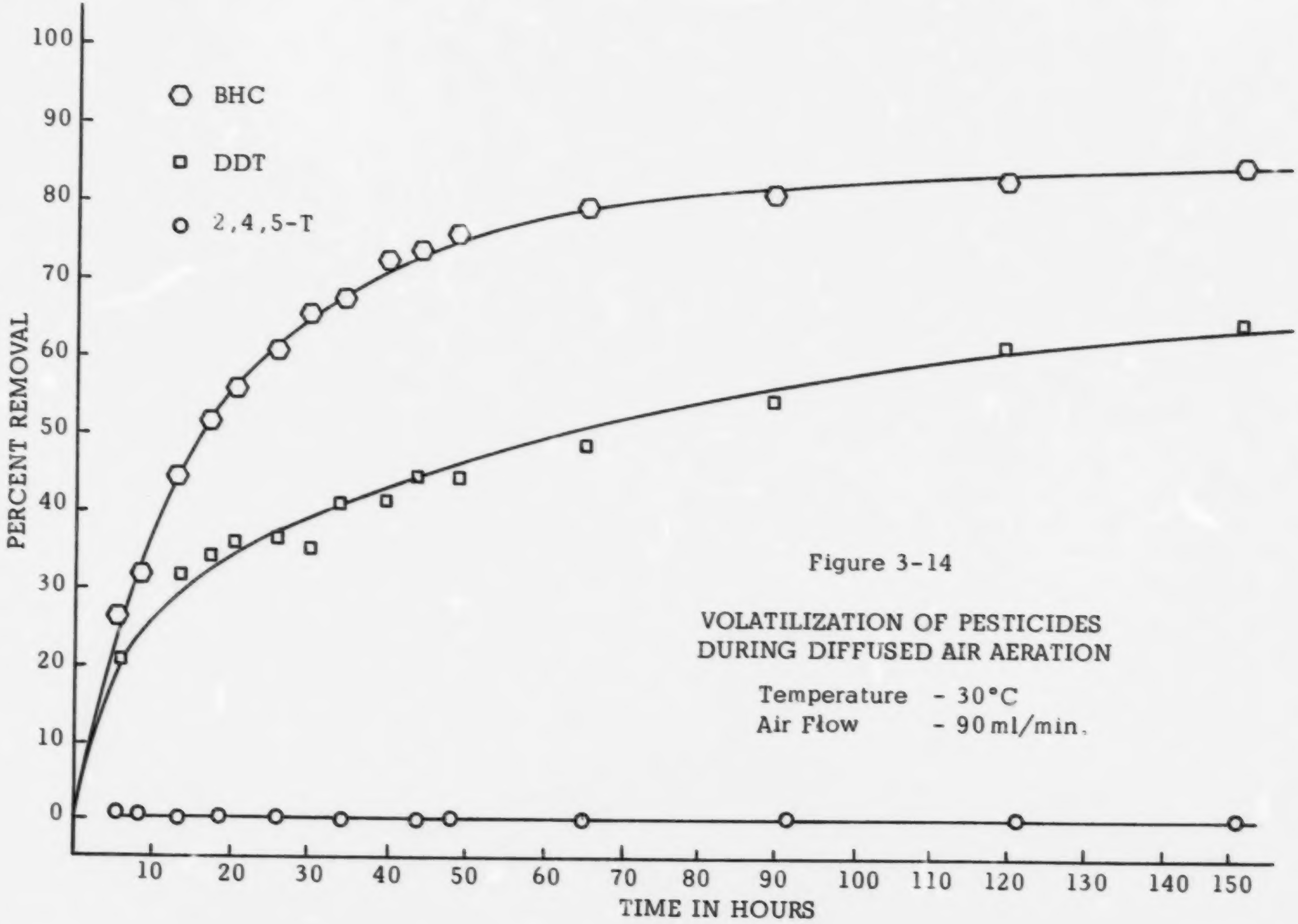


Figure 3-14

VOLATILIZATION OF PESTICIDES
DURING DIFFUSED AIR AERATION

Temperature - 30°C
Air Flow - 90 ml/min.

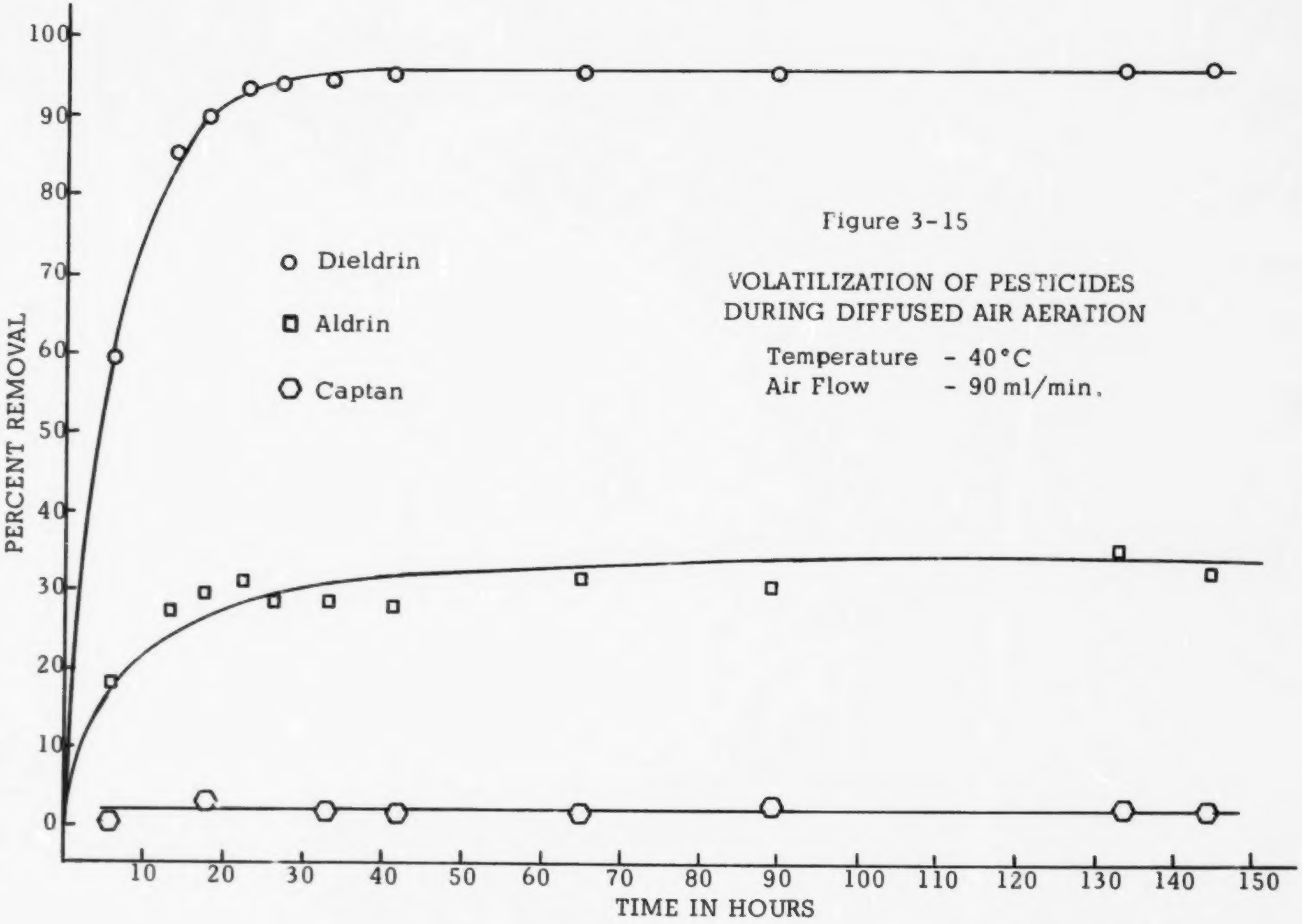


Figure 3-15

VOLATILIZATION OF PESTICIDES DURING DIFFUSED AIR AERATION

Temperature - 40°C
Air Flow - 90 ml/min.

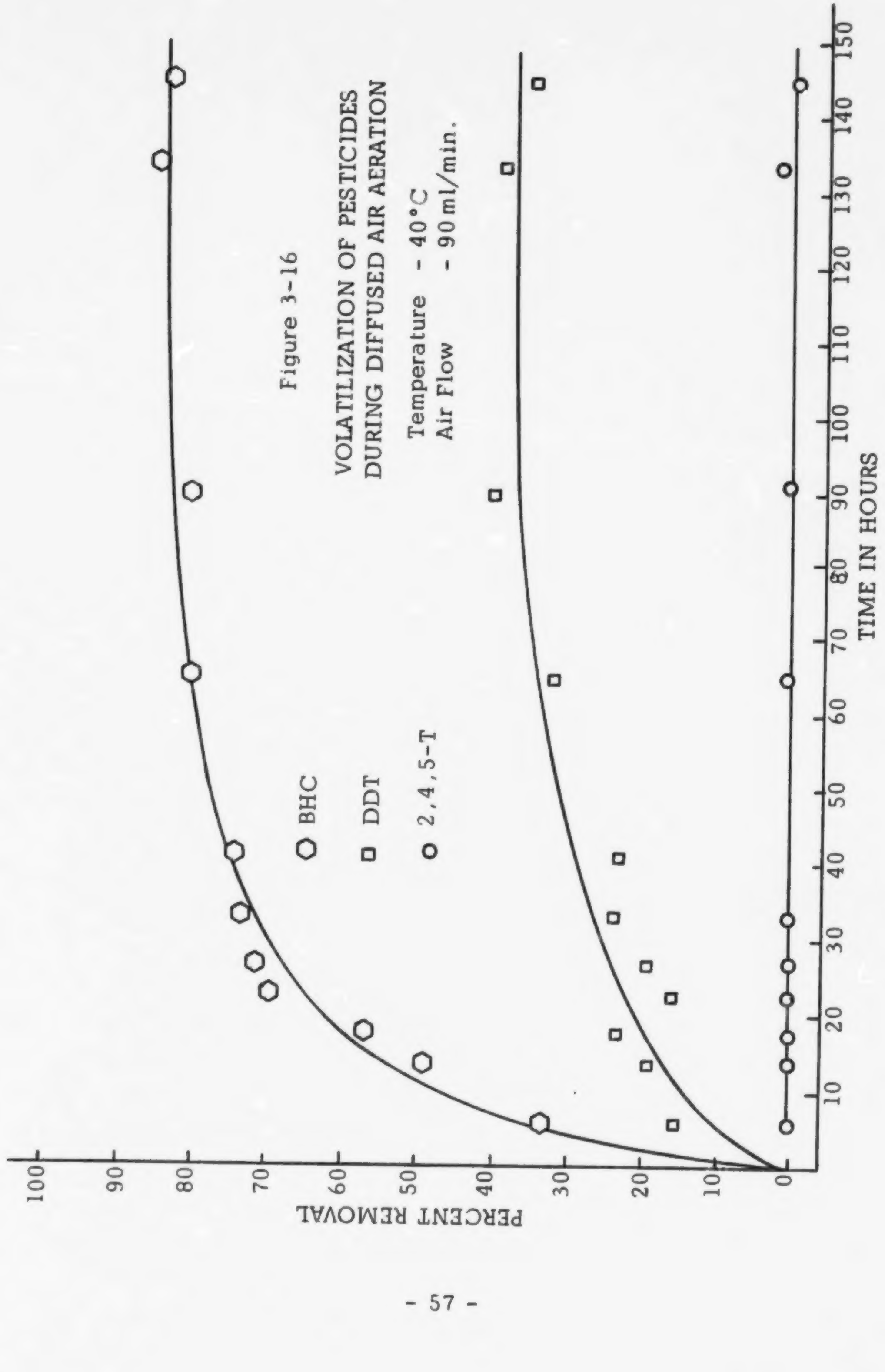


Figure 3-16

VOLATILIZATION OF PESTICIDES DURING DIFFUSED AIR AERATION

Temperature - 40°C
Air Flow - 90 ml/min.

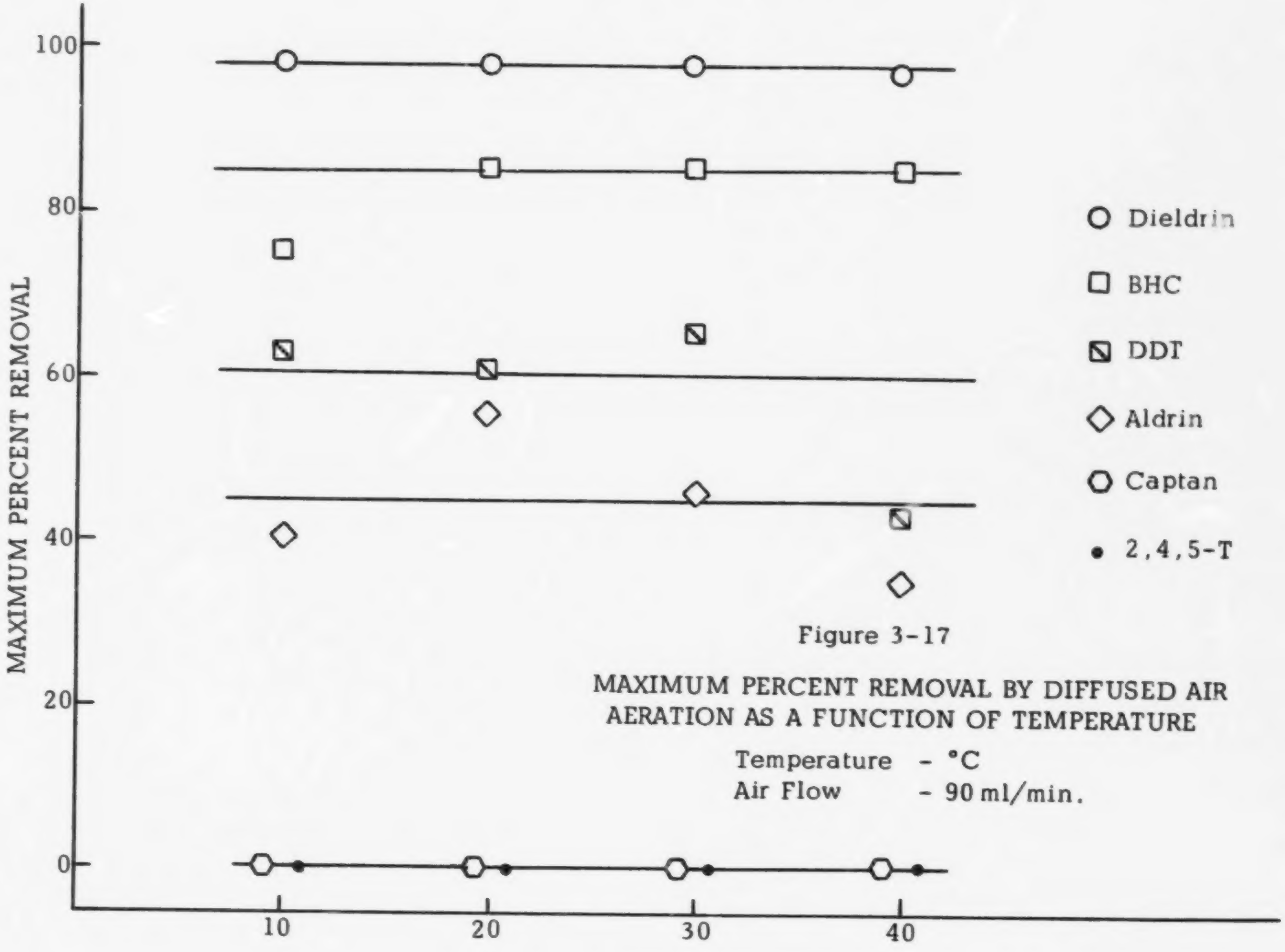


Figure 3-17

MAXIMUM PERCENT REMOVAL BY DIFFUSED AIR AERATION AS A FUNCTION OF TEMPERATURE

Temperature - °C
Air Flow - 90 ml/min.

CHAPTER IV

THE REMOVAL OF PESTICIDES FROM WATER BY CHEMICAL COAGULATION

One of the first reports of investigations concerning the removal of pesticides from water by chemical precipitation was made by Carollo (15) in 1945. This investigation concerned the removal of DDT from water supplies. Carollo used two analytical methods for this study, a bioassay technique and a chemical analysis. He found that mechanical flocculation with alum followed by sedimentation removed 40 percent of the DDT from water containing 0.1 mg/l and 50 percent at concentrations of 1.0 to 10.0 mg/l. Substituting ferric chloride or ferric sulfate removed 60 percent at 0.1 mg/l and 80 percent at 1.0 to 10.0 mg/l.

Alum coagulation, sedimentation, and filtration with filter paper increased the removals to 84 and 95 percent for the low, 0.1 mg/l, and the high 1.0 to 10.0 mg/l, concentrations of DDT, respectively. Addition of ferric chloride or ferric sulfate to this same process increased the removals to 80 and 97 percent respectively for the low and high concentrations.

Coagulation, sedimentation, and filtration followed by the addition of 1.65 mg/l of activated carbon removed essentially

100 percent of the DDT at a concentration of 1.0 mg/l provided the activated carbon was first filtered out, but the activated carbon applied with the coagulant was not so effective. Quiescent contact with activated carbon for 24 hours did not result in removal of the DDT.

The filtration of clear water through sand, anthrafilt, diatomaceous earth, sodium zeolite, or amberlite did not reduce the concentration of DDT sufficiently to prevent lethal effects on the bioassay organisms. Concentrations of 0.1 and 1.0 mg/l were used in this phase of the study. However, filtration of clear water containing 0.1 mg/l of DDT through a cation and then an anion Amberlite filter removed all of the DDT, but some of the DDT passed the beds at higher concentrations.

It should be noted, as Carollo pointed out, that the DDT present in the water was in the form of a suspension because of its low solubility in water. It was shown that, as might be expected, a large portion of the DDT suspension might be removed by the standard water treatment processes of coagulation, sedimentation, and filtration Carollo further stated that this type of treatment apparently did not remove any DDT which was in solution or in colloidal suspension, but the removal of all the DDT both in suspension and in solution was accomplished with the addition of activated carbon. Studies were not conducted on water containing DDT only in solution form.

Nicholson (49) in 1962 reported on a study that he conducted on a river system in Alabama that drained some 400 square miles of cotton farms On the area of land that was being used to grow cotton, pesticides, particularly toxaphene, DDT, and lindane, were intensively used. Toxaphane and lindane were detected in the river water while DDT was not. Nicholson also analyzed treated water from a municipal water plant that utilized a standard alum, lime process and the river as a source of raw water and found that the levels of pesticides detected in the river were not decreased by the water treatment process. The levels of toxaphene and lindane detected were 0.4 ppb and 0.75 ppb respectively.

In 1964 Robeck et.al. (51) reported on the effectiveness of water treatment processes on the removal of pesticides from water. Conventional treatment, utilizing a 20 gpm pilot plant with coagulation, followed by rapid sand filtration produced a wide variety of results. The authors explained that probably the reasons for these differences was due to the variations in solubility and the affinity for surfaces of the different pesticides. With an original concentration of 10 ppb the reported percent removed was as follows:

Lindane	Less than 10
Dieldrin	55
DDT	98
Parathion	20
2,4,5-T ester	63
Endrin	35

The addition of softening with lime and soda ash did not improve on the removal, in fact DDT and dieldrin were not as readily removed.

In 1965 Aly and Faust (50) reported on tests that they had conducted at Rutgers University in which the removal of the herbicide 2,4-D by coagulation was studied. The materials used in this study were the sodium salt of 2,4-D, the isopropyl ester of 2,4-D, and the butyl ester of 2,4-D. They concluded that the method of treating water by chemical coagulation and oxidation by chlorine and potassium permanganate will not remove 2,4-D herbicides from water. Tests were also conducted with activated-carbon treatment which was found to be an effective method of removal.

The Removal of Malathion by Chemical Coagulation

In these investigations the removal of malathion from water by nine different combinations of chemical treatment was studied. These treatments were:

a. chemical coagulation with aluminum sulfate

b. chemical coagulation with ferric sulfate

c. chemical coagulation with alum and five different polyelectrolytic coagulant aids

d. adsorption by activated carbon alone and in conjunction with coagulation with alum

e. adsorption by montmorillonite clay alone and in conjunction with coagulation with alum

For alum coagulation, reagent grade aluminum sulfate having the formula $Al_2(SO_4)_3 \cdot 18H_2O$ was used. The ferric sulfate used contained seventy-two percent $Fe_2(SO_4)_3$.

The coagulant aids used were:

Aid A - Hagan Coagulant Aid No. 18, an anionic polyelectrolyte produced by the Calgon Company (8)

Aid B - Hagan Coagulant Aid No. 50, a cationic polyelectrolyte (9)

Aid C - Hagan Coagulant Aid No. 223, an anionic polyelectrolyte (10)

Aid D - Wisprofloc 20, an anionic polyelectrolyte produced by the Isaac Chemical Company (11)

Aid E - Separan AP30, a cationic polyelectrolyte produced by the Dow Chemical Company (12)

In each test the amount of coagulant aid used was that recommended by the manufacturer (8,9,10,11,12).

For the carbon adsorption tests, Aqua Nachar powdered activated carbon manufactured by the West Virginia Pulp and Paper Company was used (13). The clay which was used was montmorillonite.

For the jar tests, a stirring apparatus accommodating six jars was used. Four 500 ml samples of stock solution were placed in 1,000 ml beakers and samples were stirred for one minute at a paddle speed of approximately 100 rpm while the chemicals were being added At the end of the one minute rapid stirring period, the paddle speed was reduced to a level sufficient to keep the chemical in suspension and stirring was continued for thirty minutes. At the end of the floculation period, the stirrers were stopped and the samples were allowed to settle for thirty minutes.

In the studies using carbon and clay, the jar test procedure was repeated twice. In the first series, carbon or clay alone was placed in the solution; 200 mg/l of alum was added in the second series

Following sedimentation, 50 ml of the supernatent were drawn off and filtered. The pH of each sample was then adjusted to 6.0 and the samples were placed in sealed flasks and refrigerated until the malathion analysis was performed. A sample of the stock solution used was also adjusted to pH 6.0 and tested for malathion content to determine the original amount of the insecticide in solution Each of the tests were duplicated to verify the results.

The amount of malation removed from solution by several reactants is shown in Figure 4-1. The combined treatment of activated carbon adsorption and alum coagulation achieved the greatest removal with forty-four percent of the malathion removed from solution at a dose of 400 mg/l.

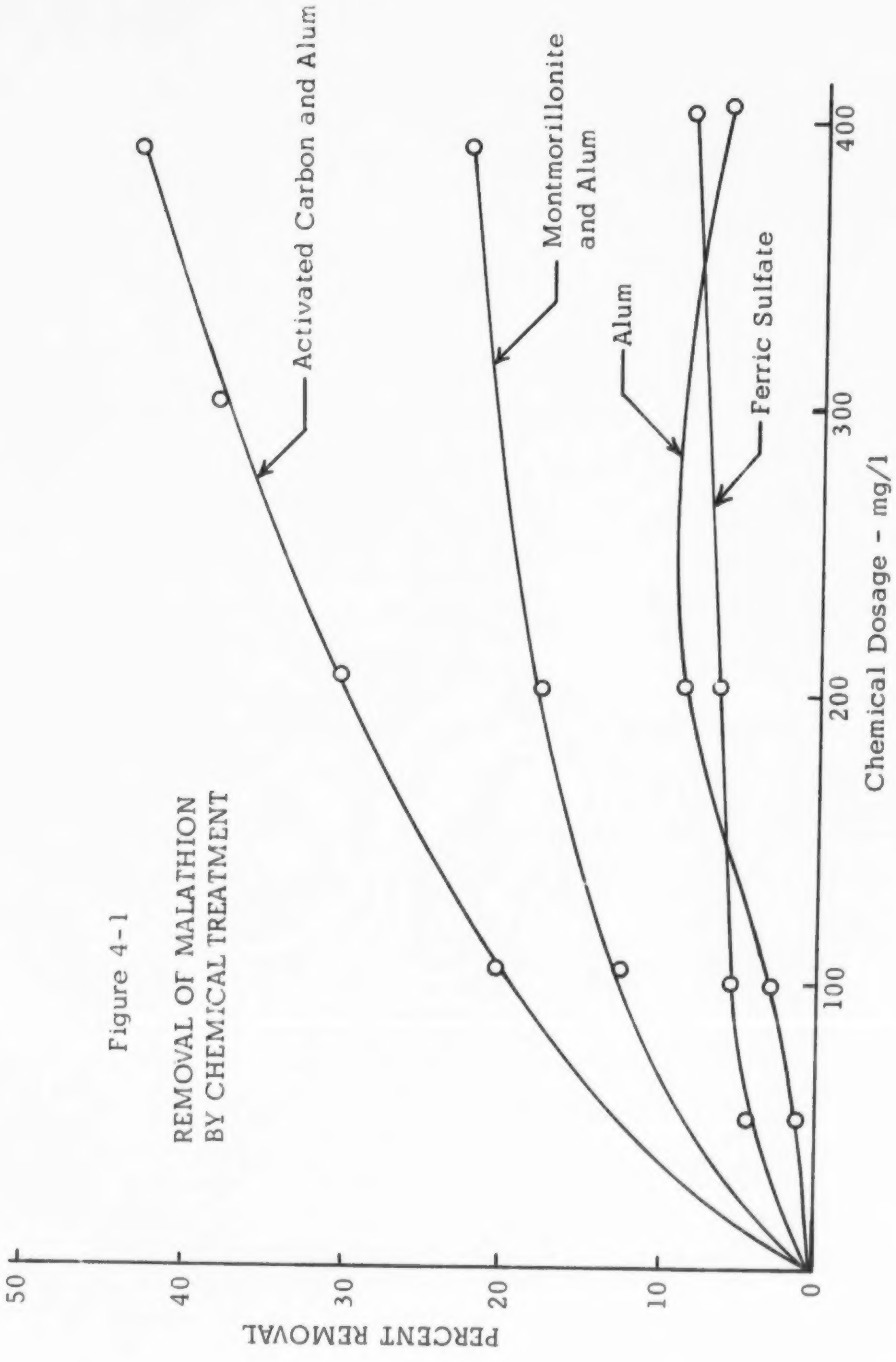


Figure 4-1

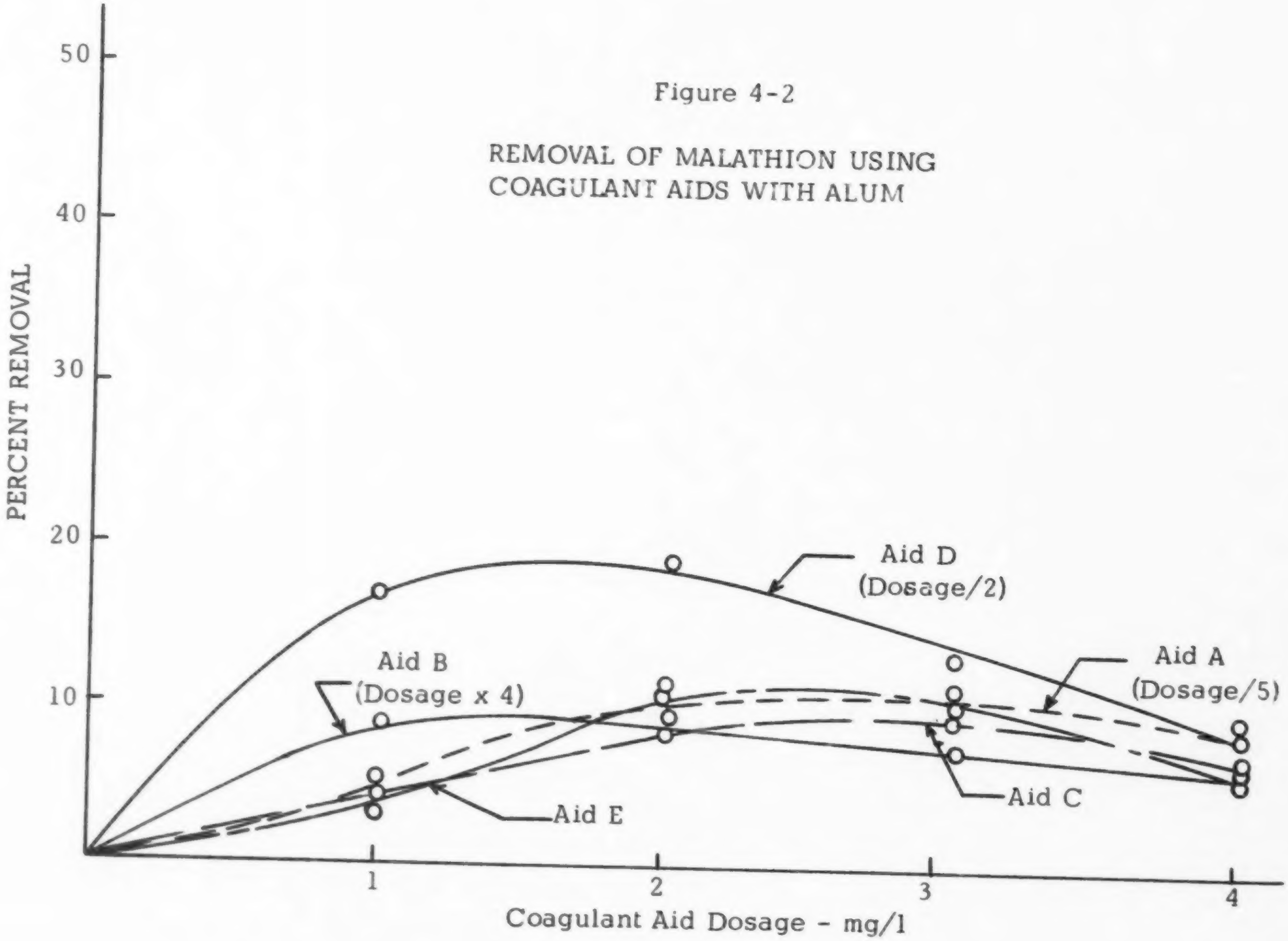
REMOVAL OF MALATHION BY CHEMICAL TREATMENT

The malathion removal accomplished by montmorillonite and alum treatment, as shown in Figure 4-1, was not as great as with the activated carbon treatment; twenty-one percent of the malathion residue was removed by a dosage of 400 mg/l. The coagulating chemicals, aluminum sulfate and ferric sulfate, were relatively ineffective in the removal of malathion. During the alum experiments the pH was in the range of 4.4 to 6.0 for all samples and in the ferric sulfate experiments, the pH was 3.5 for the 200 mg/l sample and 4.3 for the 100 mg/l sample. It can be observed from Figure 4-1 that the most effective malathion removal by alum occurred at a dosage of 250 mg/l, approximately the dosage which Black (14) found most effective for normal alum coagulation. The ineffectiveness of chemical coagulation in removing malthion from solution is probably related to the relatively high solubility of malthion in water.

Coagulant aids, when administered with 200 mg/l of alum as shown in Figure 4-2, had little effect upon the malathion removal. The amount of malathion removed by 200 mg/l of alum was 8.5 percent, and in most of the experiments with coagulant aids the amount of malathion removal accomplished ranged from 8.0 to 12 percent. The one exception was the experiment using Aid D, an anionic polyelectrolyte, in which twenty percent removal of malathion was accomplished. Since the

Figure 4-2

REMOVAL OF MALATHION USING COAGULANT AIDS WITH ALUM



other anionic coagulants used did not cause increased malathion removal and the composition of coagulant Aid D is not known, no explanation can be offered for this difference.

The Removal of DDT, Aldrin, Dieldrin, Captan, and BHC by Chemical Coagulation

The objective of these tests was to determine if the pesticides under investigation could be removed from water by chemical coagulation. Aluminum sulfate was used as the coagulant in these tests without coagulant aids, since in the previous tests with malathion the coagulant aids did not increase the removal obtained significantly. In preparing mixtures of pesticides to be tested, selected amounts of radioactive stock solutions, distilled water, and a solution of hard water were mixed to provide mixtures of each pesticide that contained 10, 100, and 250 mg/l ($CaCO_3$) hardness. The dosage of aluminum sulfate ($Al_2(SO_4)_3 . 18H_2O$) was varied from 0.02 to 1.0 grams per liter.

Each of the mixtures was tested in a manner similar to the procedure followed in the tests with malathion. Six beakers containing the pesticides in water with the desired hardness were placed on the mixers and mixed at a paddle speed of 100 rpm for one minute while the alum was added. The speed was then reduced to 20 rpm and mixing continued for 30 minutes, after which the stirring was discontinued and the floc was allowed to settle. The supernatent was decanted from each beaker, centrifuged, and samples withdrawn for counting. The percentages of pesticides removed at different dosages were calculated and are presented in Figures 4-3 through 4-5. As is evident from the data, within the range of dosage of alum used, the dosage was not a major factor in the removal obtained. In addition, the large variation in the hardness (10 to 250) of the samples used in the study did not seem to affect the removal to any great extent. The data obtained for DDT at a coagulant dosage of 10 ppm was very erratic and is therefore not presented.

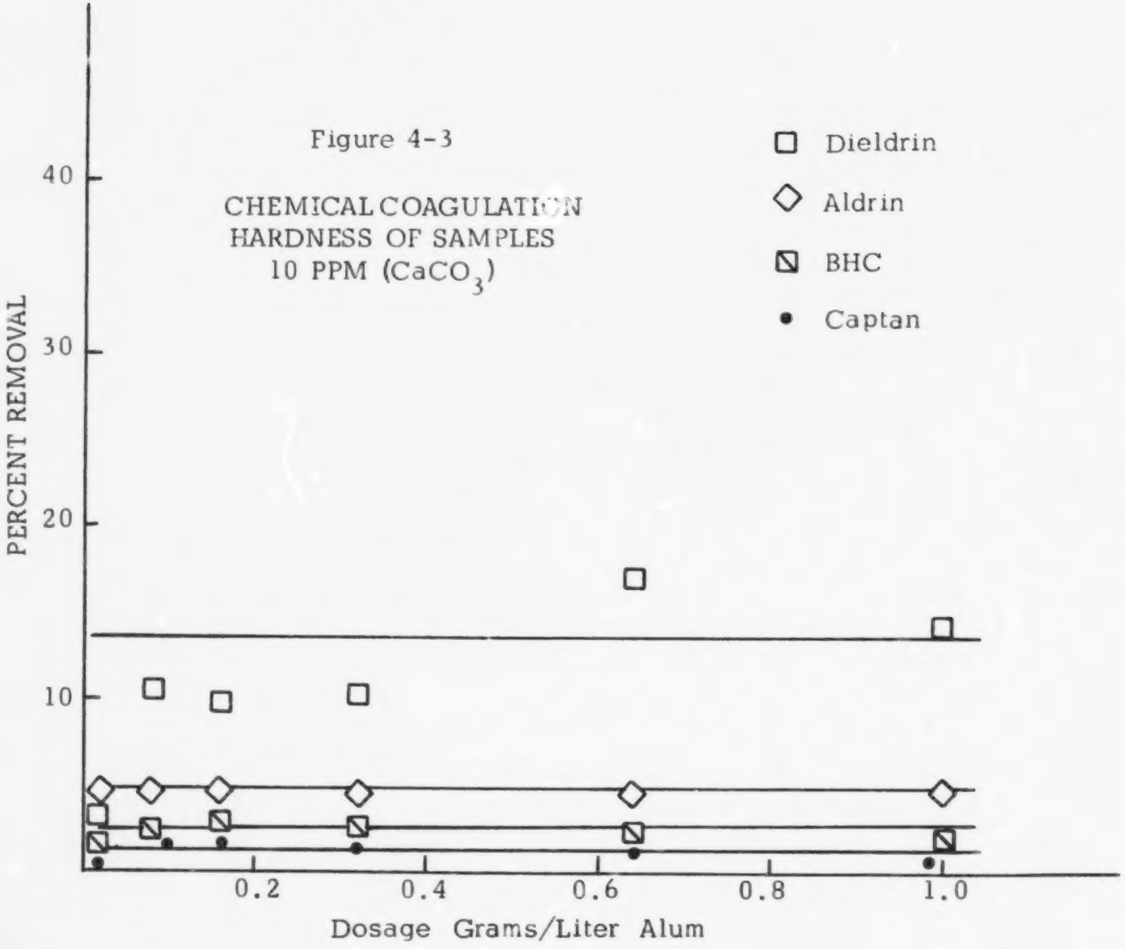


Figure 4-3

CHEMICAL COAGULATION
HARDNESS OF SAMPLES
10 PPM ($CaCO_3$)

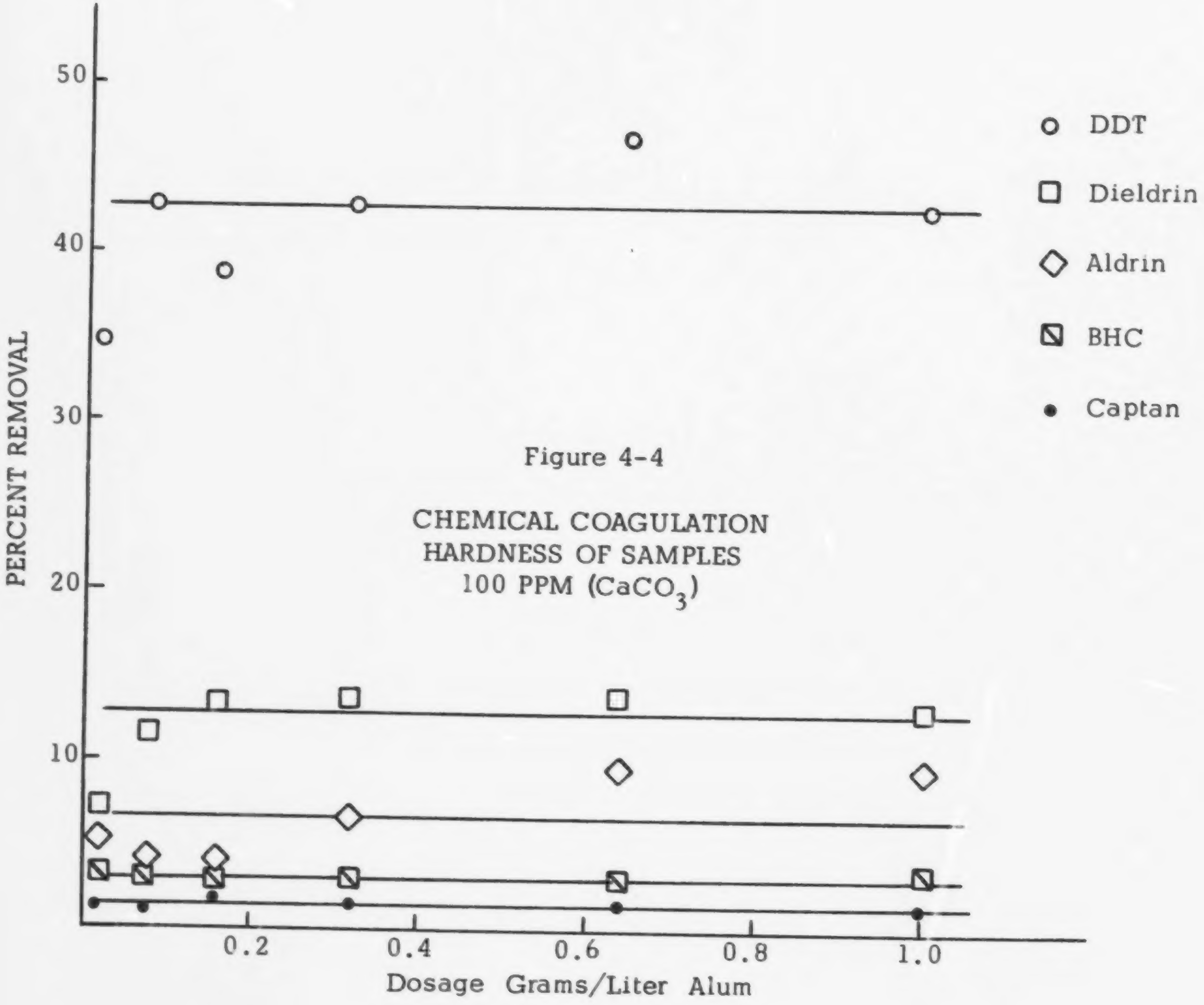


Figure 4-4

CHEMICAL COAGULATION
HARDNESS OF SAMPLES
100 PPM ($CaCO_3$)

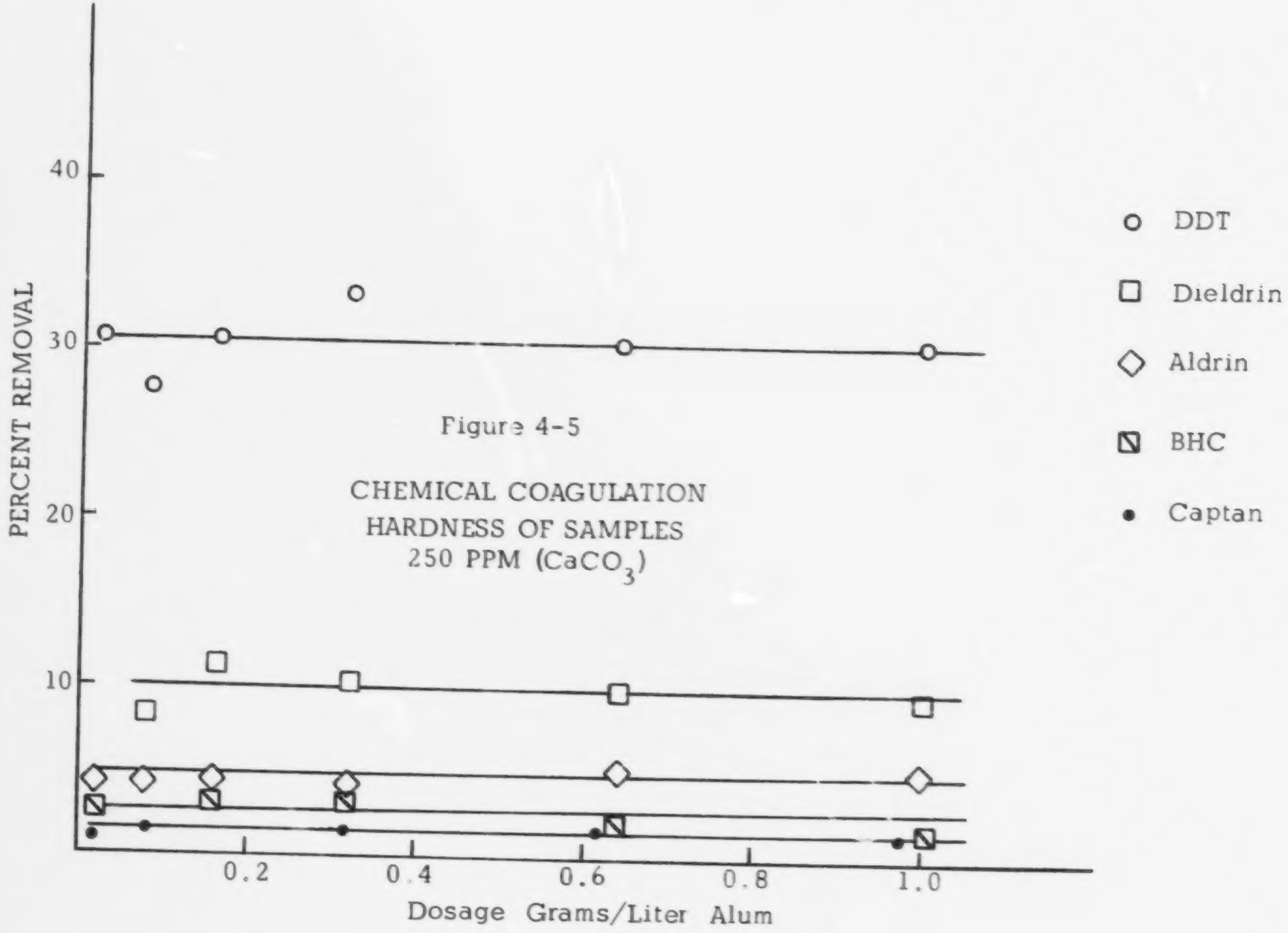


Figure 4-5

CHEMICAL COAGULATION
HARDNESS OF SAMPLES
250 PPM ($CaCO_3$)

CHAPTER V

THE REMOVAL OF PESTICIDES FROM WATER BY ADSORPTION WITH ACTIVATED CARBON AND CLAYS

In 1960, Cohen et.al. (16) reported on the removal of fish poisons from water supplies. The principal toxic agents in fish poison formulations which are in common use to kill undesirable fish are rotenone and toxaphene. The laboratory investigations which were made on these compounds and their components consisted of removal by activated carbon, chemical detoxification by chlorine and chlorine dioxide, and removal by alum coagulation.

The investigations showed that alum coagulation failed to remove either rotenone, toxaphene or the commercial formulations. Concentrations as high as 100 mg/l of alum produced no significant reduction in concentrations of the poisons. Chlorine treatment was used because it has been observed that rotenone is easily oxidized when exposed to air and light. Investigations showed that 41.5 mg/l of chlorine with a 15 minute contact time would be required to reduce the toxicity of 0.1 mg/l rotenone to one half the 36-hr TL_m. Toxaphene showed no reduction in toxicity when treated with 200 mg/l chlorine for 180 minutes using an initial concentration of 0.3 mg/l toxaphene. This was as expected because toxaphene is a highly chlorinated hydrocarbon.

Chlorine dioxide offered a promising method of treatment because rotenoid compounds are particularly sensitive to oxidation and chlorine dioxide, expressed on a weight basis and in terms of available chlorine, has theoretically, 2.5 times as much oxidizing capacity as chlorine. This proved to be very effective in that 0.88 mg/l of chlorine dioxide applied to a 0.1 mg/l solution of rotenone for 15 minutes reduced the toxicity to one-half the 96-hr TL_m for fish or 0.003 mg/l. However, chlorine dioxide dosages as high as 7.9 mg/l had no effect on 0.3 mg/l toxaphene, even after a contact time of 180 minutes.

Activated carbon provided the best removal of the fish poisons investigated because it was the only treatment which produced significant removal for each of the poisons. It might also be preferred over chlorine and chlorine dioxide because it will also eliminate odors which might be objectionable. The amount of carbon required to produce removal of 0.3 mg/l of both toxaphene and rotenone to one-half TL_m was about eight to ten mg/l.

Cohen (17) also noted in a later report on the same field project at Dickinson, North Dakota, that activated carbon dosages which will reduce the odor of organic solvents used in the formulation of fish poisons to a favorable level will also reduce the toxic concentrations to a safe level. Thus, he concluded that removal of odor also removed the pesticide residue.

Leopold, et al (18) reported in 1960 on investigations on removing 2,4-D and similar herbicides from water by activated carbon. This study attempted to show the relation between the molecular structure of the herbicides and the herbicide adsorption on activated carbon. Adsorption was measured by radioactivity on the carbon following exposure to 2,4-D tagged at the carboxyl carbon. The carbon used in these investigations was an adsorbing medium activated carbon prepared by the Atlas Powder Company.

The influence of pH on the adsorption of 2,4-D was examined over a buffered range of 2.2 to 8.0. It was found that within this range there was a uniform adsorption.

A summary of these investigations as stated by Leopold et.al. (18) is given below

> "The adsorption onto carbon was measured for 17 of the chlorinated derivatives of phenoxyacetic acid. It was found that one, two and three chlorine substitutions in the phenyl ring increased the adsorption properties of the molecule. A strong inverse correlation between the adsorption and solubility was found, phenoxyacetic acid being the most soluble and least adsorbed of the series, and successive chlorinations decreasing solubility and increasing adsorption onto charcoal."

In 1962, Schwartz (19) reported on the removal of 2,4-D from prepared simulated Missouri River water. This study consisted of developing a rapid laboratory technique for determining the pesticide concentrations in water and evaluating the effectiveness of coagulants, coagulant aids used in conjunction with coagulants, and activated carbon in removing pesticide residues from water. A brief summary of the results of this study is presented below.

1. A procedure involving chloroform extraction followed by ultraviolet adsorption measurements was developed as an analytical technique for measuring 2,4-D concentrations above 3 mg/l.
2. Radioactive 2 4-D provided a very accurate and sensitive means of measuring extremely low concentrations of 2,4-D.
3. Only three to six percent of an initial 2,4-D concentration of 10 mg/l was removed by the natural silt, and optimum removal was accomplished at pH values in the range of 3.
4. Ferric sulfate coagulation and aluminum sulfate did not significantly increase the maximum amount of 2,4-D (range 3 to 15 mg/l) removed from the test water over that obtained by silt alone, and the optimum pH for removal by these methods was 7.0.
5. There was no increase of removal with the use of coagulant aids with ferric sulfate. In fact the anionic

coagulant aid actually reduced the removal from that obtained with the coagulant alone.

6. Activated carbon is an efficient method of removing 2,4-D at concentrations which might be expected in a water supply. At 2,4-D concentrations of 10 mg/l, a significant portion, 60 percent, was removed by an activated carbon dosage of 100 mg/l. Almost complete removal, more than 99 percent, was obtained at low 2,4-D concentrations, 0.1 mg/l, with an activated carbon dosage of 50 mg/l. Optimum removal of 2,4-D with activated carbon was accomplished at pH values in the range of 3.

As Schwartz pointed out, 2,4-D concentrations that would be expected in water supplies would be lower than many of the test concentrations used in the study and could be removed almost completely.

Extensive studies on adsorption by activated carbon have been made by Weber and Morris (20),(21). In the first study by Weber and Morris (21) the adsorbates used were sodium benzene sulfonate, nitrochlorobenzene, and dichlorodiphenyltrichlorothane (DDT). The first of these is the active ingredient in household detergent and the other two are chlorinated hydrocarbon compounds used in agriculture and industry.

Ultraviolet spectrophotometry was used as the analytical method for the determination of solute concentration. Batch treatment, in which the carbon and the adsorbate are shaken together, was the procedure followed throughout the study. The principal objective was to determine which factors governed the rate of adsorption. The factors considered were pH, carbon particle size, concentration of carbon, time, temperature, and molecular size and configuration of the adsorbate.

From their studies, Weber and Morris (21) concluded that the overall rate of adsorption appears to be controlled by the rate of diffusion of solute within the micropore structure of the granulated carbon. Most of the factors considered had some effect on the rate of adsorption, for example, relative rates were found to vary reciprocally as the square of the diameter of the individual carbon particles for a given weight of carbon. This indicates that the particle size should be kept as small as possible to produce the best adsorption.

One of the most important portions of the study concerned examination of the effect of concentration of solute on the rate of adsorption. The rate was determined to be a linear function of the square root of the concentration within the range of experimentation.

However the ratio of concentration at time "t" to concentration at time zero was found to decrease more rapidly with "t" the more dilute the solution. In dilute solution, a greater fraction of solute was adsorbed per unit time although the total quantity of solute adsorbed per unit time was less. This would be an important factor in the effectiveness of the adsorbent for removing pesticide residues since concentrations involved are generally small.

Molecular size and configuration of the adsorbate was found to have a definite effect upon the rate of adsorption on granular carbon. This rate decreased considerably with increasing size of the adsorbate. Molecules having highly branched structures have been shown to be removed much more slowly than those of identical molecular weight but of such configuration as permits coiling and attainment of compactness resulting in high rates of diffusion into the pores of the carbon.

The rate of uptake of alkyl benzene sulfonate by carbon was found to increase with decreasing pH of the solution. Weber and Morris (21) concluded that the increase in rate observed for decreasing pH may be due to alterations in the carbon surface with changing hydrogen ion concentration. They stated:

> "A decrease in pH quite probably results in reduction of the negative charges at the surface of the carbon, thus enhancing the adsorption of the negatively charged alkyl benzene sulfonate."

This might indicate that some further treatment of the activated carbon may be possible such as to make it even more effective as an adsorbent.

The second study of Weber and Morris (20) involved the evaluation of the suitability of adsorption as a unit operation for treatment of waters and waste waters. The report of this study includes the results of experimental investigations on the equilibria of adsorption of typical organic pollutants on carbon, of the capacity of carbon for adsorption, and of factors that govern capacities and positions of adsorption equilibria.

The organic substances for which the equilibria of adsorption on carbon from aqueous solutions have been investigated include nitrochlorobenzenes, several alkylbenzene sulfonates of different molecular weight and configuration, phenol, dichlorodiphenyltrichlorothane, and some alkylphenoxypolyethoxyethanols. The factors which have been found to affect capacities of adsorption include the particle size of the adsorbent, the temperature, and the pH.

The results of this investigation indicated that adsorbates of a high molecular weight are adsorbed to a considerably greater extent than are those of low molecular weight. This was found true for compounds of similar chemical constitution.

Increasing temperature results in decreasing capacity, which might be expected, since physical adsorption is ordinarily an exothermic process. An inverse relationship between capacity and pH was observed which may be the result of changes in the charge characteristics of the carbon surface with changing pH. At low pH values negative charges on the surface would be reduced, therefore affording greater affinity for negatively charged adsorbate ions. This conclusion concerning the effect of pH is the same as was reported in the first study by Weber and Morris (21).

It was also observed that capacity of adsorption increased with decreasing particle size. This increase is undoubtedly the result of the opening of tiny, effectively sealed channels in the carbon upon breaking up a large particle into several small particles.

In 1964, Joyce and Sukenik (22) made a series of investigations using granular, activated carbon in both bed-packed columns and batch tests to remove much of the organic matter, including alkylbenzene sulfonate (ABS) from municipal waste water. The carbon used for the batch tests was pulverized to a 95 percent, 325-mesh size and added to either 500 or 1,500 milliliter volumes of ABS solution in Erlenmeyer flasks. This solution was agitated for two hours before being filtered and the ABS content determined. The columns used for the tests were 1-inch-diameter Pyrex pipe sections packed with granular, activated carbon. Three different flow rates were used with bed depths ranging from 2.5 to 15 feet, and break-through curves were established at each flow rate by collecting samples from each column section at intervals and determining the ABS content. The authors concluded that by including a reactivation process to permit re-use of the carbon the amount of carbon required for counter-current contacting is less than one pound per 1000 gallons of waste treated. With reactivation, the total cost of carbon adsorption was estimated to be less than ten cents per 1000 gallons for plants treating 10 mgd of waste water.

In 1964, Robeck et.al. (51) reported on the effectiveness of powdered activated carbon on the removal of pesticides from water. Tests were conducted with various pesticides ranging in concentration from 1 ppb to 10 ppb. The pesticides were added to distilled water and also to raw Little Miami River water and duplicate tests run on each. Due to the organic material in the raw water a larger dosage of carbon was required with it than with distilled water to obtain a similar removal. It was determined that two step treatment with activated carbon was more economical than attempting to obtain the required removal in one dosage. The results of these studies are summarized in Table 5-1.

TABLE 5-1 (51)

PARTS PER MILLION OF ACTIVATED CARBON REQUIRED TO REDUCE THE PESTICIDE LEVEL IN DISTILLED WATER AND IN LITTLE MIAMI RIVER WATER

Pesticide	Method	10 ppb*		1.0 ppb*	
		1.0†	0.1†	0.1†	0.05†
Parathion	JT‡	2.5	5	0.5	0.6
	P§	5	10	0.9	1.1
2,4,5-T ester	JT	2.5	17	1.5	3
	P	14	44	3	5
Endrin	JT	1.8	14	1.3	2.5
	P	11	126	11	23
Lindane	JT	2	12	1.1	2
	P	29	70	6	9
Dieldrin	JT	3	12	1.1	1.7
	P	18	85	7	12

*Initial level of pesticide.

†Pesticide level after treatment.

‡Jar test, in which pesticide is removed from distilled water by activated carbon alone, with a contact time of an hour.

§Plant treatment, in which pesticide is removed from river water by conventional treatment and activated carbon.

Principles of Adsorption on Activated Carbon

Activated carbon may be thought of as a solid foam, that is, a porous interior with a large surface area within a rigid granule or particle structure of relatively small volume. This type of structure may be developed by heating or chemically treating organic materials of cellular structure such as woody products or bone. Activation of this type of material by means of heat is essentially a process of destructive distillation in which a part of the material is driven off in the form of volatile products. This process leaves a carbonaceous residue which has a large volume of internal voids. A similar result is achieved by chemical activation, accomplished usually by treatment with zinc chloride or phosphoric acid supplemented by heat.

Carbons may be classified on the basis of the raw materials from which they are derived. Thus, carbons suitable for adsorption from solution may be divided into carbons of animal origin and carbons of vegetable origin. Carbons of animal origin are commonly designated as bone char while the raw materials used in the manufacture of vegetable carbons are lignite, wood charcoal, and the black ash residue which is a by-product of paper manufacturing. Another raw material which is becoming quite popular in the manufacture of vegetable carbon is cocoanut shell.

Bone char is commonly used in the refining of sugar and has been used as such since the early part of the nineteenth century. Freshly made bone char usually contains only about ten percent carbon and is thus usually not nearly as effective as vegetable carbon because effectiveness is related to carbon content. Bone char is generally losing its place in the cane sugar industry although the beet-sugar industry still uses it almost exclusively.

Vegetable carbons are increasing in use, primarily because of their application with large volumes of liquids containing low concentrations of impurities. These carbons differ from bone char in that the carbon content usually ranges from 75 to 90 percent, and they are much softer. The bulk density of vegetable carbons is usually only about 30 percent that of bone char. The most wide-spread use of vegetable carbons is in the removal of substances which cause tastes and odors in water.

The primary characteristic of an activated carbon which is to be used as an adsorbent is that it have a large surface area per unit weight. Other variables that enter into the adsorption process include temperature, pH, time, particle size, and dosage. The general rule has been to conduct the adsorption process at as high a temperature as the nature of the liquid will permit. This, however, is not in agreement with the studies conducted by Weber and Morris (20) in which they determined that adsorption of the alkylbenzene sulfonates on carbon was decreased with increasing temperature. However except for a few specific cases it is generally accepted that in practice the adsorption increases with temperature. It is also generally accepted that the governing factor of the temperature variable is the viscosity of the liquid, which is reduced by an increase in temperature (23). This reduction in viscosity allows increased penetration of the liquid into the submicroscopic capillary structure of the carbon.

The rate at which the adsorption process progresses is also affected by the pH of the solute. It is generally stated that carbons adsorb more effectively in acid solutions than in alkaline solutions, but this generalization should not be used as a criterion without qualification merely because it has been often correct for industrial applications of carbon. The idea that carbons adsorb better in acid solution than in alkaline, such as is the case in many industrial applications, arises from the fact that above pH 9.5-10.0 many adsorbable substances are hydrolyzed. When these substances are hydrolyzed, many of them undergo simplification of physical and chemical structure which reduces adsorbability. The principal effect of pH on the process of adsorption on activated carbon appears to be indirect, through its influence on the solubility of the adsorbate (23). The general rule is that maximum adsorbability is generally associated with minimum solubility which most often occurs in the alkaline pH range.

Adsorption has been described as a substantially instantaneous process; but when powdered carbon is added to a liquid solution, time is required to reach adsorption equilibrium. Powdered carbon generally has a particle count expressed in billions per gram and each of these suspended particles must be considered to have a definite "sphere of adsorption" several times greater in volume than the volume of the particle itself (23). Thus, this particle must move about this sphere under the influence of a stirring action in order to bring about the full reduction in concentration of solute of which the extent and nature of its area is capable. Therefore, the contact time required to reach equilibrium is inversely proportional to the dosage of carbon used. It is also for this reason that a relatively longer contact time is required in practice for carbons of high adsorptive capacity than those of lower capacity to achieve a given result. Smaller doses of the higher capacity carbons are required to achieve a given amount of adsorption and thus a relatively longer period of time is required for the smaller number of particles to move through the liquid and produce the maximum possible reduction in adsorbate concentration.

Particle size is a variable of the adsorption process which is related to the need for a large surface area per unit weight and to the equilibrium adsorption time. Development of a large surface area may be achieved by grinding a given weight of carbon to produce more particles, which creates a greater surface area per unit weight. Particle size is also related to the equilibrium adsorption time, in that a given weight of smaller sized carbon will reach equilibrium more quickly than the same weight of the same carbon of larger sized particles. Thus, the particle size variable may be considered to be important even though it is related closely to other variables.

In a liquid-phase application, the transfer of the adsorbate from the bulk solution to the carbon particle must advance through at least two stages. The first stage is the transfer of the adsorbate molecule from the bulk liquid to the surface of the carbon particle. Next, the migration of the adsorbate from the surface of the carbon to the adsorption surface within the particle (25). Since it is known that the first step in his process takes place much more rapidly than the latter step, it would seem that the latter step is the rate controlling factor in the process. Thus, it would seem that the rate of adsorption would vary with the diameter of the carbon particles.

The carbon dosage is a variable in the adsorption process which is closely related to the surface area and particle size. When equal volumes of a liquid containing an adsorbable impurity are contacted with different weights of an activated carbon, the distribution of that impurity between the adsorbed and solution phases will depend on the amounts of carbon present. Therefore, with larger dosages of the same carbon there is a greater chance of contact in a shorter period than with smaller dosages.

EXPERIMENTAL STUDIES OF ADSORPTION ON ACTIVATED CARBON

Studies With Malathion

The purpose of this investigation was to determine the effectiveness of activated carbon in removing malathion, an organic phosphate insecticide, from water.

Tests were conducted with 95% pure malathion mixed with distilled water to concentrations of 5 ppm, 10 ppm and 25 ppm. All solutions of pesticide and water to be tested were prepared immediately prior to conducting the tests to eliminate the effects of the hydrolysis of the malathion. The activated carbon used was Fisher Cocoanut size 140/200 as manufactured by the Fisher Chemical Company, and the dosage ranged from 10 mg/l to 250 mg/l. The test procedure used was to place 200 milliliters of the malathion solution of desired concentration into each of nine glass stoppered 1000 ml Pyrex flasks. To these flasks the following carbon dosages were added, 0 (control flask), 10,20,30,40,50,100, and 250 mg/l.

The flasks were then all placed on a Burrell wrist-action shaker for a period of two hours. In previous studies (Figure 5-1) the equilibrium time was determined to be 1 to 1 1/2 hours; therefore, a contact time of two hours was selected for these tests. After two hours of shaking the flasks were removed and the contents of all flasks, including the control, were filtered separately through Watman No. 42 filter paper. The filtrate was then extracted with 50 ml of pesticide quality hexane and analyzed with the gas chromatograph. These results are presented in Figure 5-2. As would be expected the data shows that a larger dosage of carbon is required to effect a given removal as the initial concentration of malathion is increased. Substantially 100 percent removal of the malathion could be obtained for all the levels of malathion used.

Studies With 2,4-D

The purpose of this portion of the investigation was to study the effectiveness of several activated carbons in removing 2,4-D, a chlorinated hydrocarbon herbicide, from water.

The first portion of the investigation was designed to determine the effect of hydrogen ion concentration (pH) upon the removal of 2,4-D from solution by activated carbon. The second portion of the investigation involved an evaluation of the effectiveness of

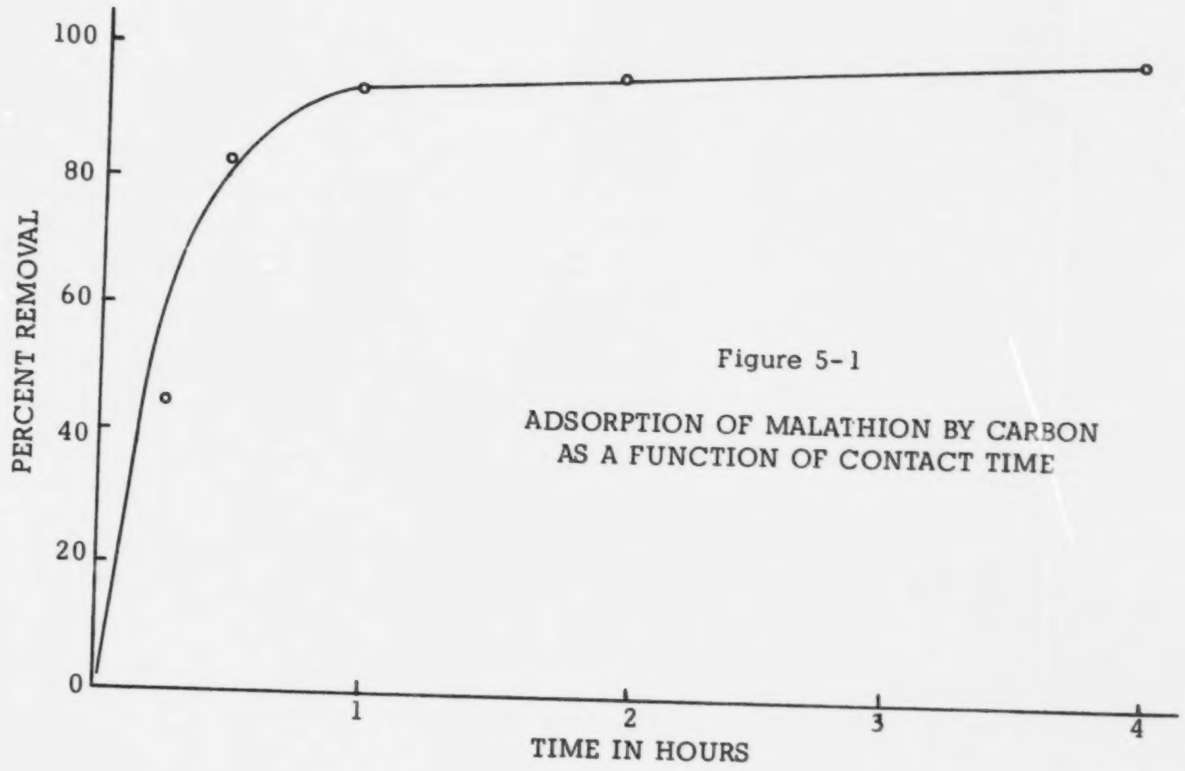


Figure 5-1

ADSORPTION OF MALATHION BY CARBON AS A FUNCTION OF CONTACT TIME

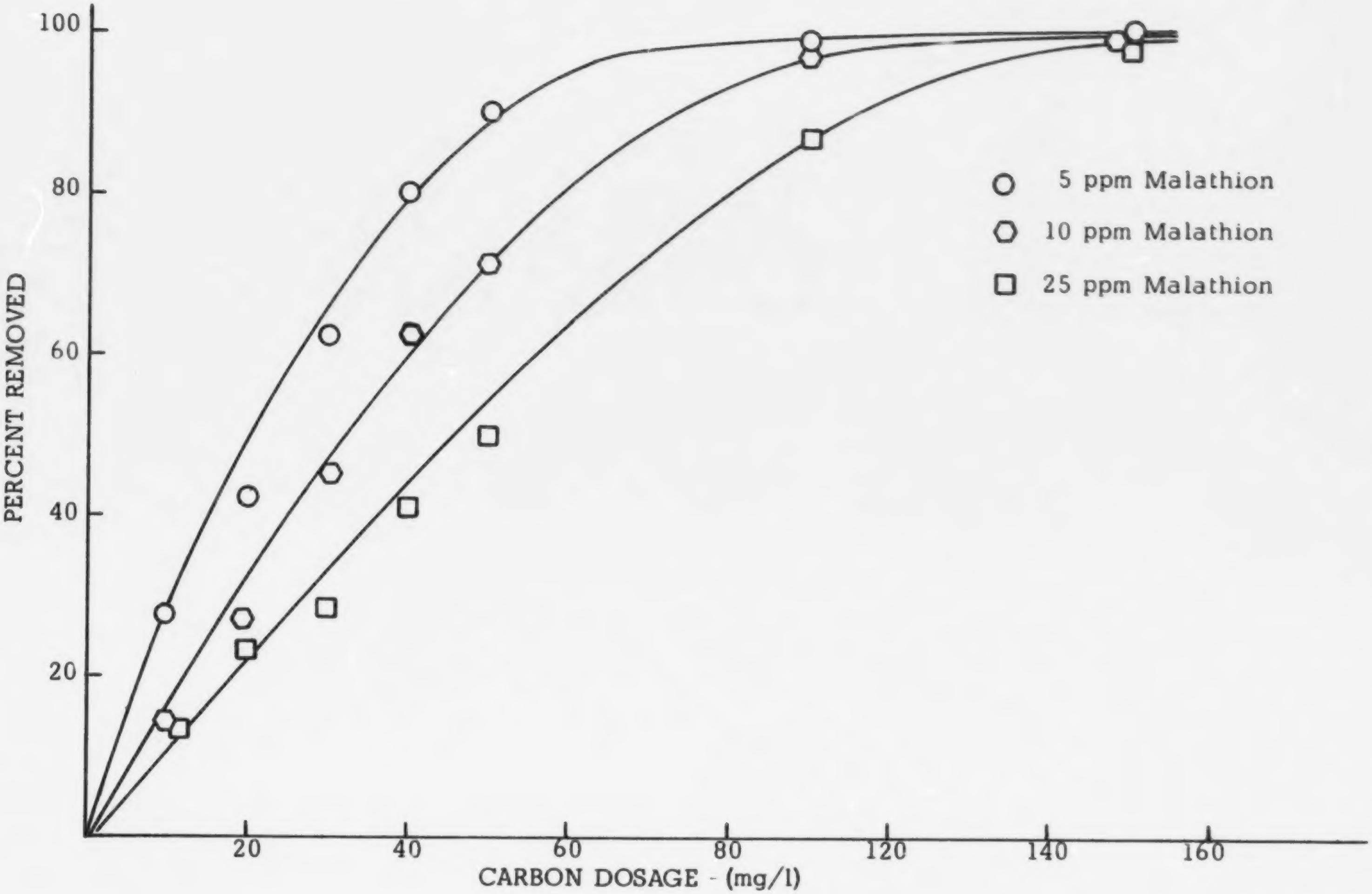


Figure 5-2
ADSORPTION OF MALATHION AS A FUNCTION OF CARBON DOSAGE

several types of activated carbons in removing 2,4-D from solution at constant pH.

Preparation of Activated Carbon

Several activated carbons were used in these tests to determine the effectiveness of adsorption of 2,4-D from a water solution. The carbons were all commercially available, pre-activated materials which were obtained from their respective manufacturers. Samples of carbons were obtained from the American Norit Company (Norit), Atlas Powder Company (Darco G-60) Barnebey-Cheney Company (Barnebey-Cheney XH-2), Cliffs Dow Chemical Company (Cliffchar R-Coarse), Fisher Chemical Company (Fisher Cocoanut and Fisher Animal) Pittsburgh Activated Carbon Company (Pittsburgh Type CAL), and West Virginia Pulp and Paper Company (Nuchar C-190 and Aqua Nuchar).

Study of the Effect of pH Upon Carbon Adsorption

A preliminary investigation showed that a greater removal of 2,4-D was accomplished by the activated carbon at low pH values than at high pH values. This result led to a study of the effect of pH on the 2,4-D in solution with no activated carbon present. The study was performed by placing 800 ml of the 2,4-D solution in a beaker and stirring vigorously as the pH was lowered in increments from 8.0 to 1.0. After each pH adjustment, the solution was allowed to stir for 15 minutes before being sampled. From this test, a range of pH values was found over which the pH had no effect on the 2,4-D in solution, and this pH was used in subsequent tests.

This study showed that above pH 4.0, the 2,4-D in solution was not affected while below pH 4.0, the 2,4-D remaining decreased rapidly with decreasing pH as shown in Figure 5-3. Less than 10 percent of the 2,4-D remained in the solution at pH 1.0, compared with 90 percent remaining at pH 3.0. It was thought that the 2,4-D perhaps was undergoing a decarboxylation reaction with the tagged carboxyl carbon coming off as CO_2. Further studies with 2,4-D with the tagged carbon in the number two position showed that this was not the case. The loss of 2,4-D from solution at lower pH values is probably due to conversion of the 2,4-D to the un-ionized free acid which is known to be fairly volatile. The apparent high removals obtained by activated carbon at low pH in these tests, as well as in tests by other investigators, is apparently due more to this factor rather than to true adsorption.

Tests were also run to show the effect the pH plays in removing the 2,4-D from solution by activated carbon. These tests were performed by placing 20 mg of carbon in flasks with 200 ml of the 2,4-D solution (100 ppm) and mixing for one hour. The pH of the

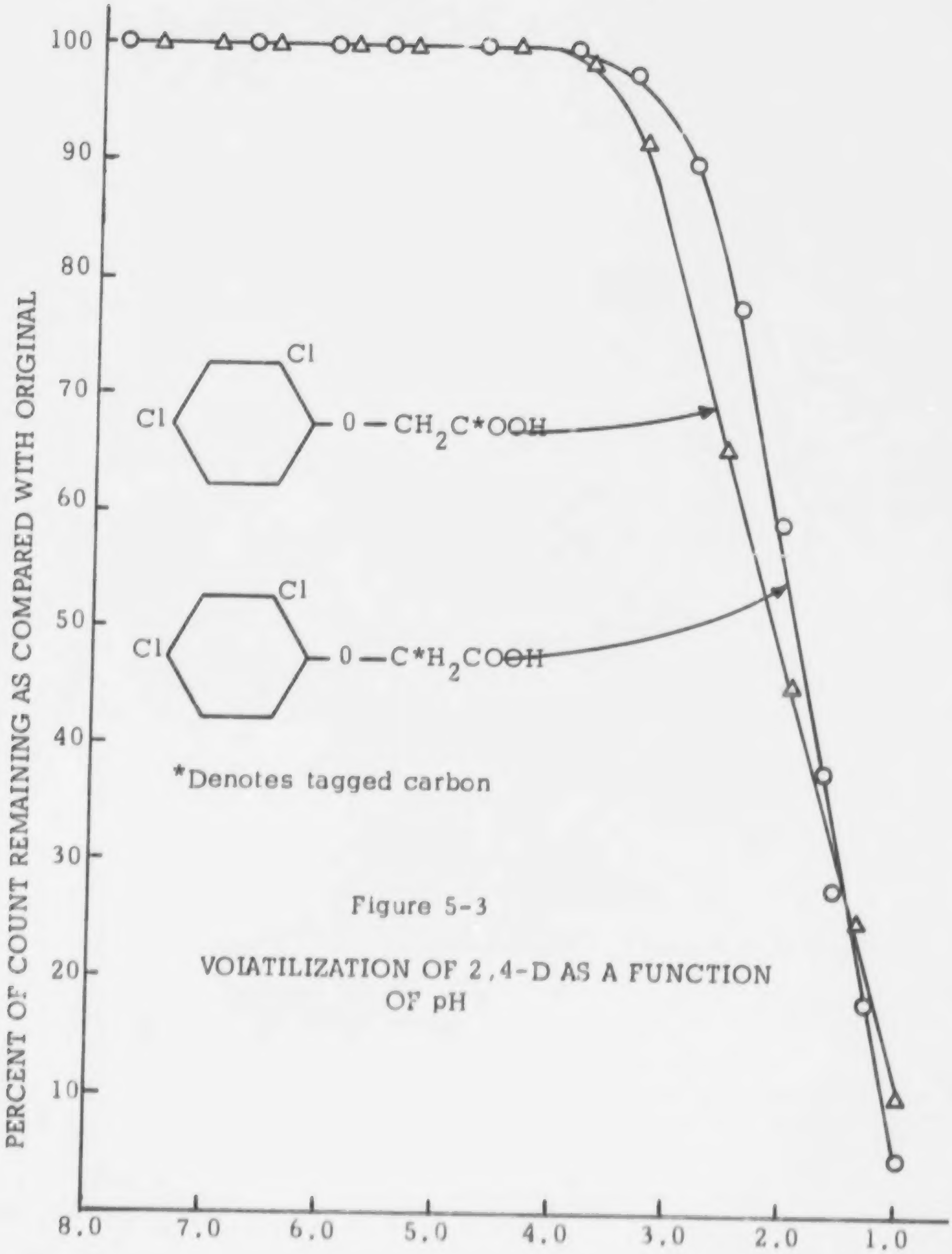


Figure 5-3

VOIATILIZATION OF 2,4-D AS A FUNCTION OF pH solution in each flask was adjusted prior to contact with the activated carbon. The pH values for this test ranged from 7.0 to 2.0 and six different values were tested.

The results of this test are shown in Figure 5-4 in which the percent 2,4-D removed is plotted against the pH of the solution. Reference should be made also to Figure 5-3 in which it was shown that the pH of the solution had no effect on the volatility of 2,4-D if the pH was above 4.0. Thus, it should be concluded that lowering the pH of the solution increased the removal of the 2,4-D by activated carbon. This agrees with Schwartz (19) but does not agree with the results of Leopold, et.al. (18) who stated that uniform adsorption takes place over a range of pH values from 8.0 to 2.2.

Study of the Effect of Contact Time Upon Carbon Adsorption

The effect of contact time was one of the variables studied in this investigation. Eight 200 ml samples of stock solution were transferred to 300 ml. flasks and 20 mg. (100 mg/l) of activated carbon was added to each flask. The pH of the stock solution was then adjusted to 6.0 and the flasks were placed on a Burrell shaker. Each sample was shaken for a specified time before being removed to be counted. Before sampling each sample was filtered to remove the activated carbon. A blank was also filtered to insure that none

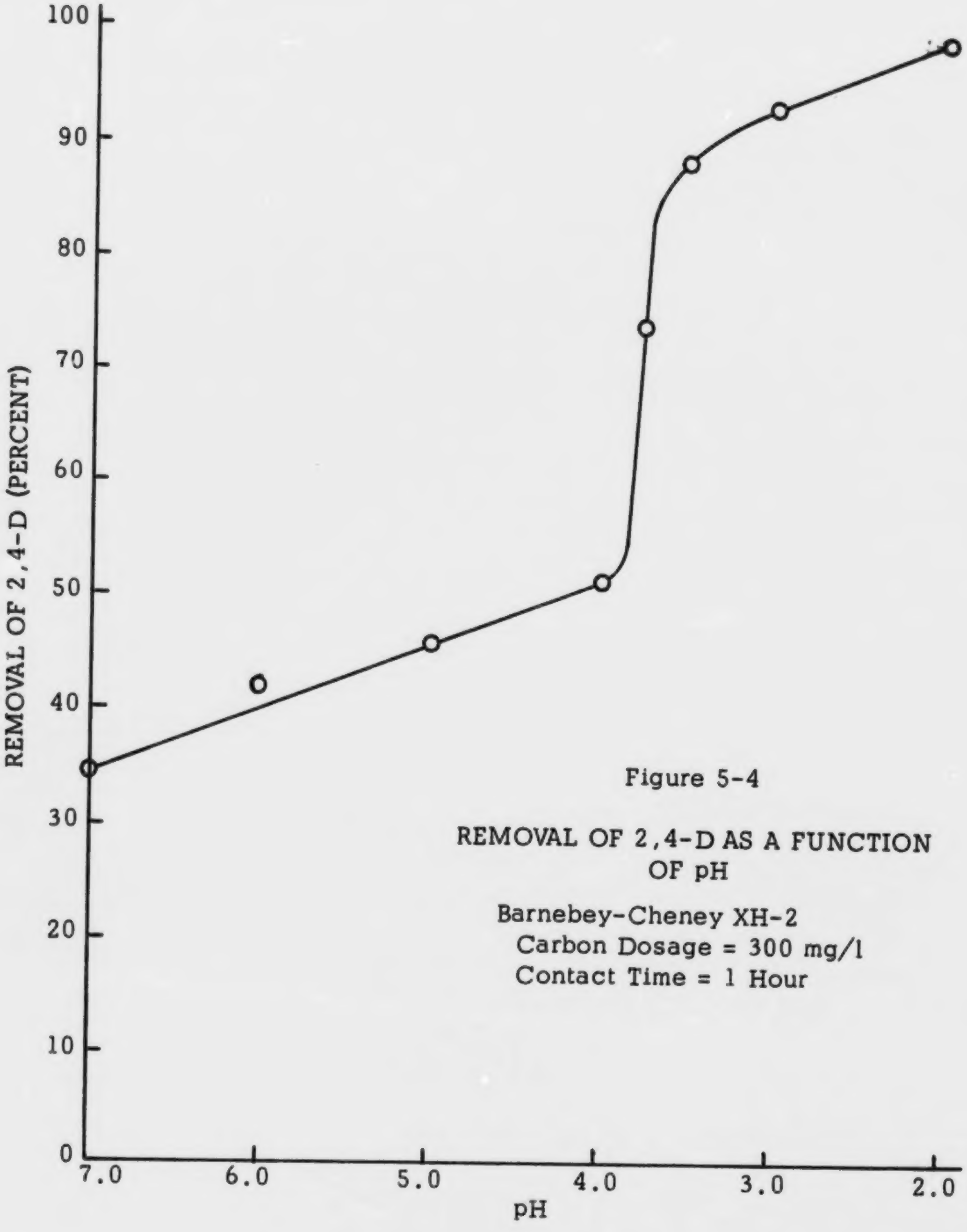


Figure 5-4

REMOVAL OF 2,4-D AS A FUNCTION OF pH

Barnebey-Cheney XH-2
Carbon Dosage = 300 mg/l
Contact Time = 1 Hour

of the solution was adsorbed on the filter. After filtering, three one-milliliter samples were obtained from which a determination of the residual amount of 2,4-D was calculated. The flasks were removed from the shaker at times of 15 min., 30 min., 45 min., 60 min., 1 1/2 hrs., 2 hrs., 3 hrs., and 4 hrs. By comparing the residual amount of 2,4-D in each flask to the amount in the stock solution, the effect of contact time was established. Separate tests were run using nine varieties of activated carbons. This experiment was duplicated for each activated carbon to check the results.

From the data shown in Figures 5-6, 5-7, and 5-8, it was observed that during the first hour of mixing, the 2,4-D was adsorbed much more rapidly than it was adsorbed thereafter. After the first hour of mixing, the rate of adsorption of the 2,4-D from solution by the activated carbon decreased rapidly, as is typical in reactions of this type. The rate of adsorption varied also with the carbon used. By observing the data, it may be seen that the rate of adsorption curves for each of the carbons were similar in shape except for the curve for Pittsburgh carbon. The Pittsburgh carbon exhibited a slower initial rate of adsorption than the other carbons tested, but after a four hour contact time this carbon had adsorbed a greater amount of 2,4-D than any of the other carbons tested except Fisher cocoanut carbon.

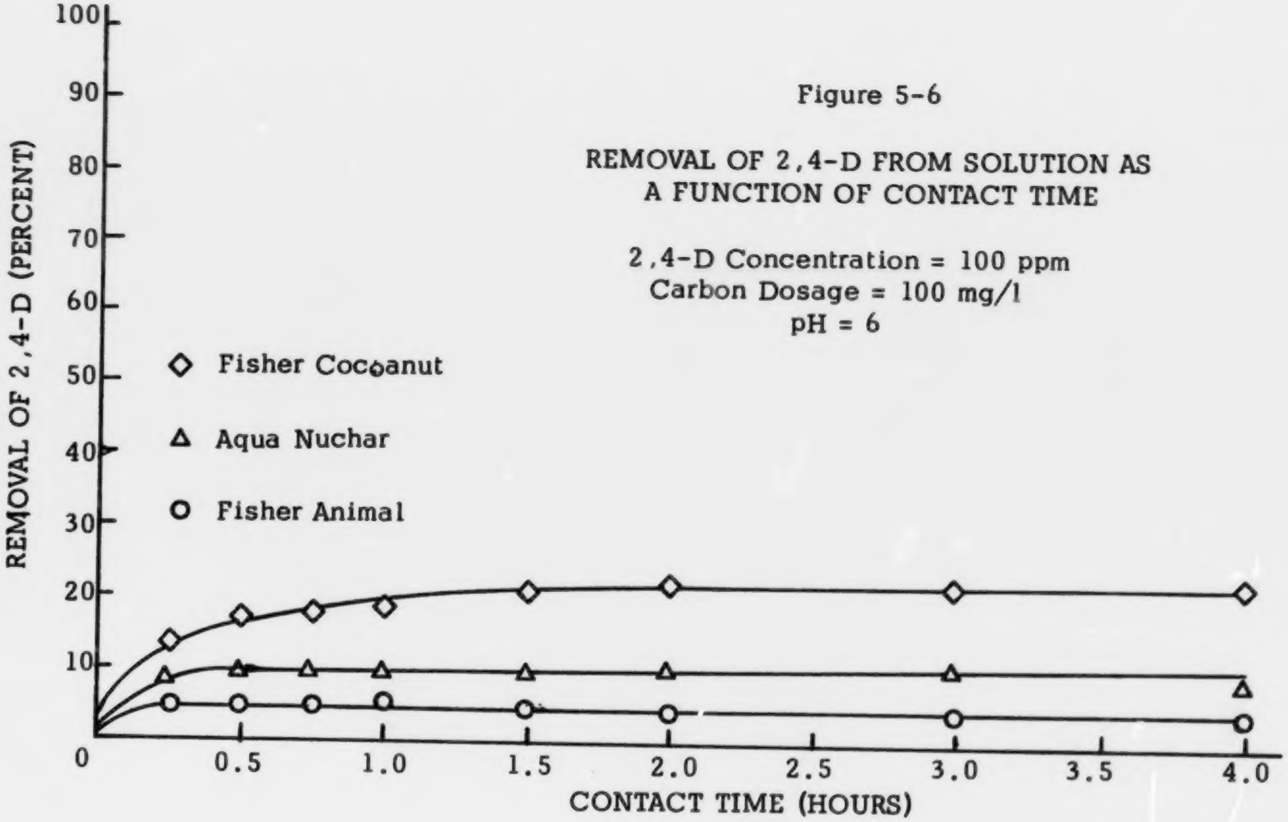


Figure 5-6

REMOVAL OF 2,4-D FROM SOLUTION AS A FUNCTION OF CONTACT TIME

2,4-D Concentration = 100 ppm
Carbon Dosage = 100 mg/l
pH = 6

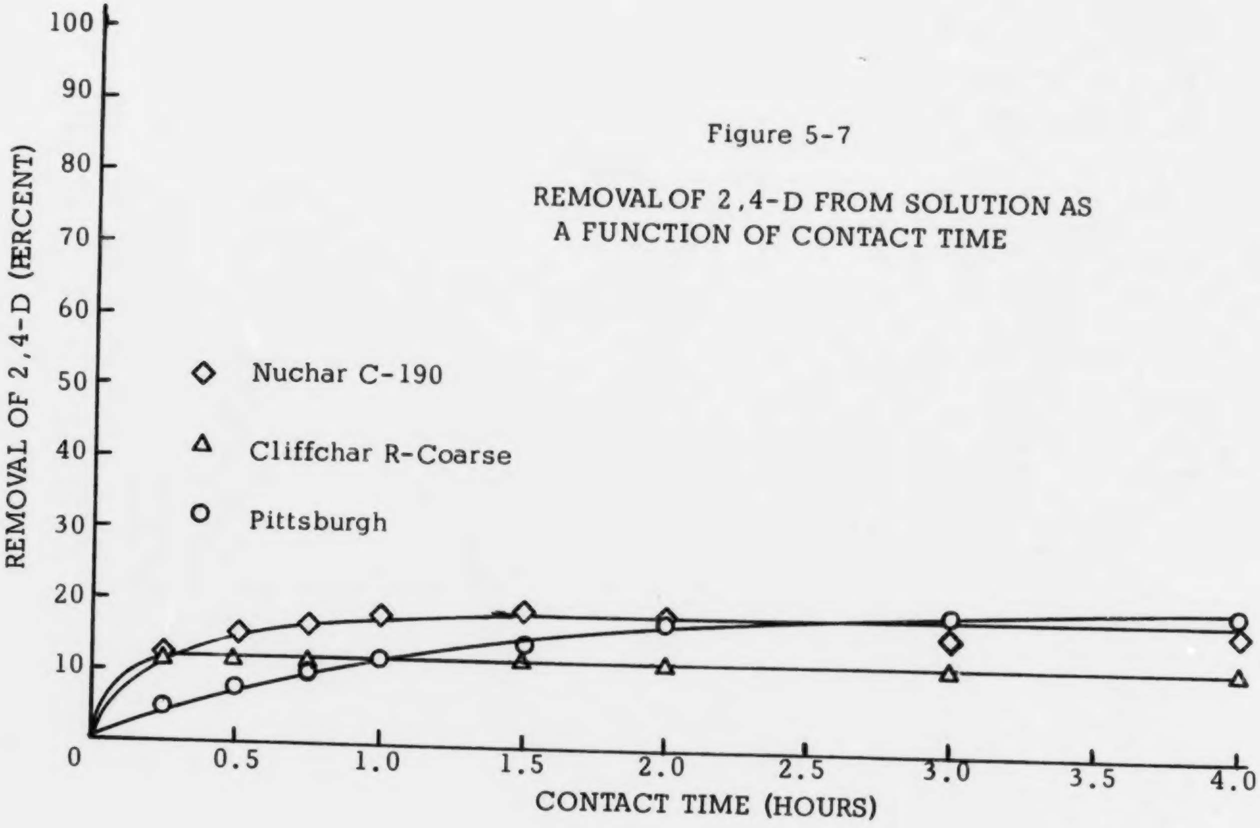


Figure 5-7

REMOVAL OF 2,4-D FROM SOLUTION AS A FUNCTION OF CONTACT TIME

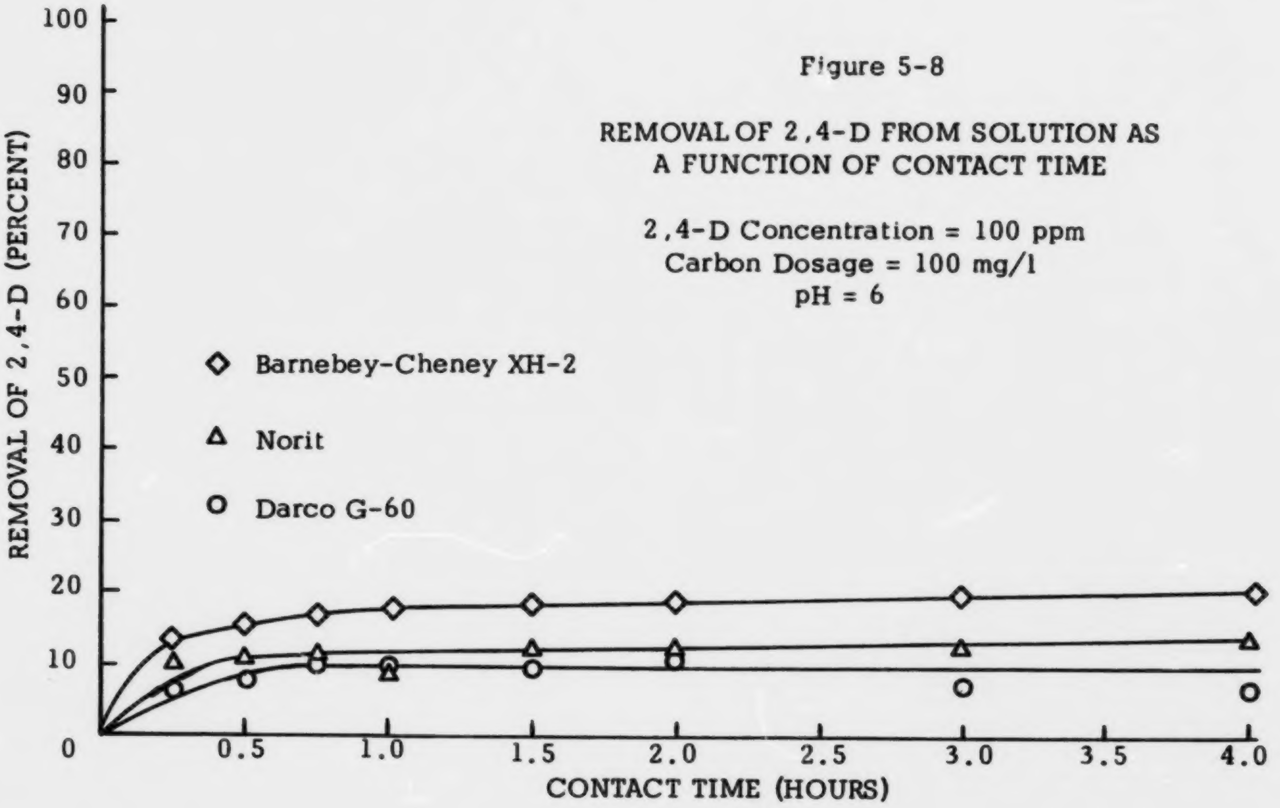


Figure 5-8

REMOVAL OF 2,4-D FROM SOLUTION AS
A FUNCTION OF CONTACT TIME

2,4-D Concentration = 100 ppm
Carbon Dosage = 100 mg/l
pH = 6

The only carbon of animal origin used in these tests showed the least adsorption of 2,4-D from solution. This was expected because of the very low carbon content in carbons prepared from this source.

Study of Effect of Carbon Particle Size Upon Carbon Adsorption

A few tests were made using activated carbon of different sizes to determine the effect of particle size on the rate and total removal of 2,4-D from water. The four sizes used were 60/80, 80/100, 100/140, and 140/200, with mean diameters of 0.213 mm., 0.163 mm., 0.127 mm., and 0.089 mm. respectively. Sixty milligrams of activated carbon were placed in a flask with 200 ml. of 2,4-D solution containing 100 ppm 2,4-D and the solution and carbon were allowed to mix. At the end of one hour, the contents of each flask were sampled to determine the amount of 2,4-D adsorbed by the activated carbon.

The results of this test are shown in Figure 5-9 in which the percent removal is plotted as a function of mean particle size. The rate of adsorption increases slightly as the mean diameter of the particles of a given weight of carbon decreases, since a greater percent of the herbicide was adsorbed in the same period of time. Decreasing the particle size of a given weight of carbon

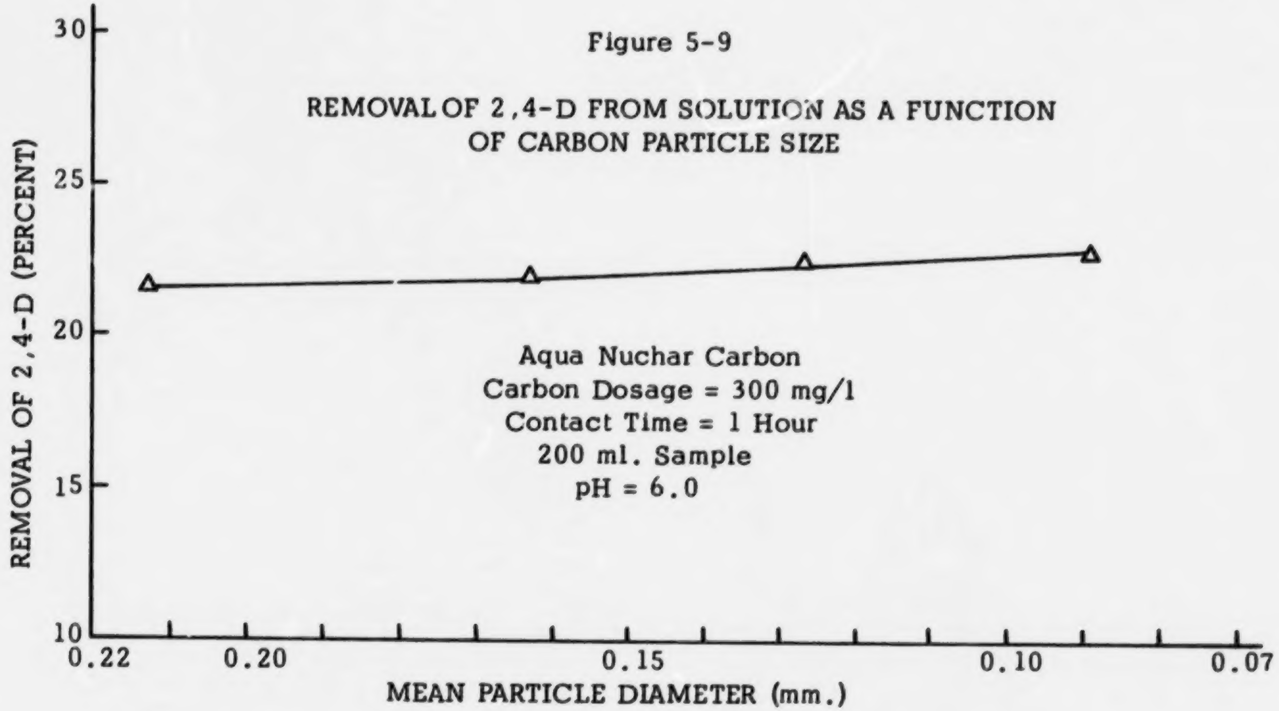


Figure 5-9

REMOVAL OF 2,4-D FROM SOLUTION AS A FUNCTION OF CARBON PARTICLE SIZE increases the surface area of the carbon and thus creates more active sites on the carbon on which the 2,4-D may be adsorbed. This increases the probability of a molecule of 2,4-D in solution coming into contact with an active site on the carbon and being adsorbed by the carbon.

Study of the Effect of Carbon Dosage Upon 2,4-D Removal

The effect of carbon dosage was studied in much the same manner as that described in the preceding section except that a variable carbon dosage was used with the time being held constant at one hour, and the pH at 6.0. Carbon dosages of 5,25,50,100,300,500, 700, and 900 mg/l were used. As before, all of the 200 ml. samples were shaken in 300 ml. flasks on a Burrell shaker. The samples were filtered to remove the carbon before the portion to be used in the determination of residual 2,4-D was drawn from the filtrate. A blank was also filtered to insure that none of the 2,4-D was adsorbed by the filter. After filtering, three one-milliliter samples were drawn from the filtrate to be used in the determination of residual 2,4-D. By comparing the residual concentration of 2,4-D in each flask to the concentration in the stock solution, the effect of carbon dosage was determined.

Figure 5-10 shows the percent 2,4-D removed from solution for varying concentrations of 2,4-D as a function of carbon dosage.

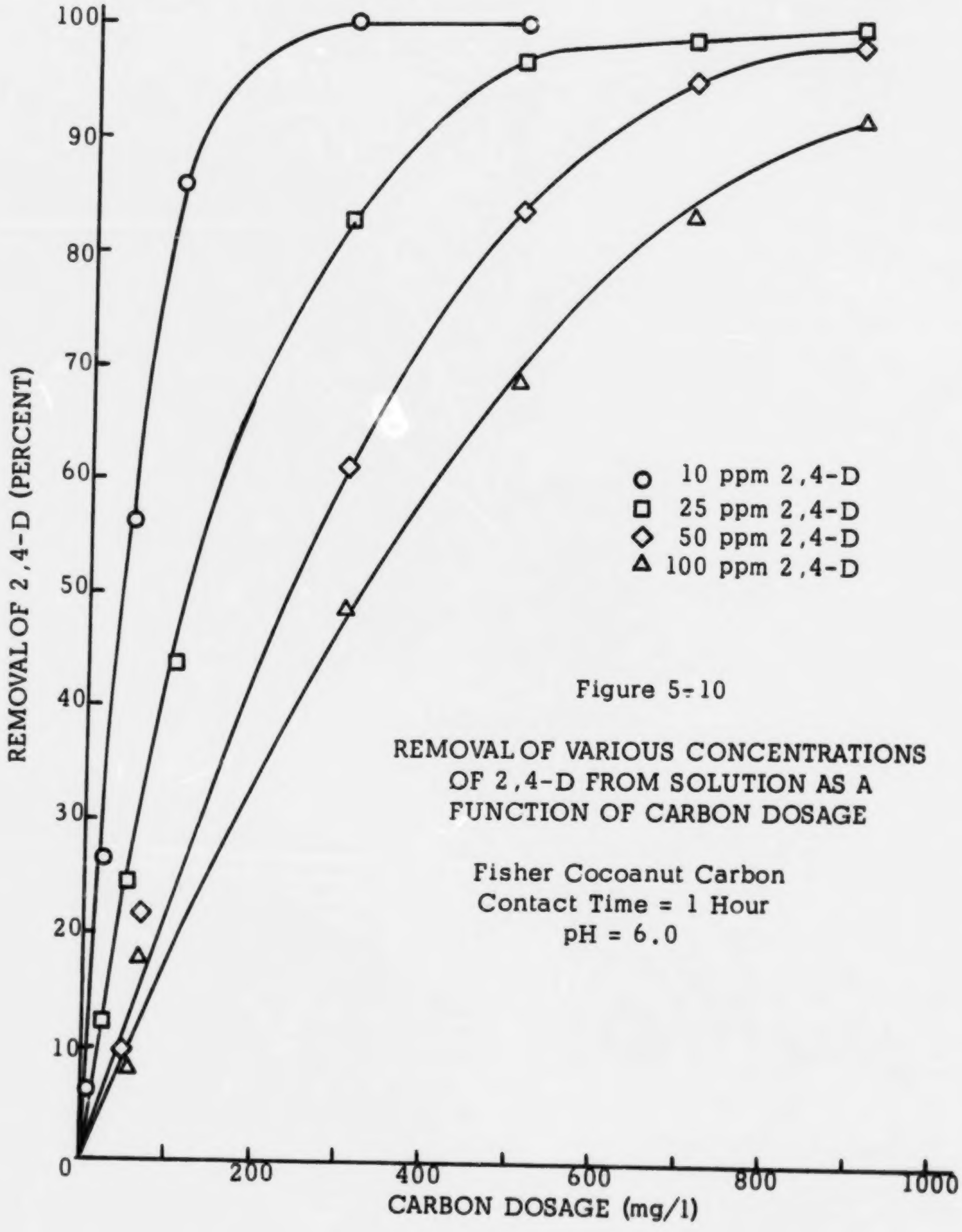


Figure 5-10

REMOVAL OF VARIOUS CONCENTRATIONS OF 2,4-D FROM SOLUTION AS A FUNCTION OF CARBON DOSAGE

Fisher Cocoanut Carbon
Contact Time = 1 Hour
pH = 6.0

It should be noted that the rate of adsorption or the quantity of 2,4-D removed from water by a given amount of carbon in a given time is much faster in the more concentrated solutions. This should be expected and is in agreement with the work done by Weber and Morris (21), which showed that the rate of adsorption is slower in dilute solutions.

Figures 5-11, 5-12, and 5-13 show the percent 2,4-D removed as a function of carbon dosage for various types of activated carbons. An original 2,4-D concentration of 100 ppm, a contact time of one hour and a constant pH = 6.0 were used in these tests.

Studies With Aldrin, Dieldrin, and DDT

The objective of this part of the study was to determine the effectiveness of activated carbon in removing aldrin, dieldrin, and DDT from water.

The initial consideration was the effect of hydrogen ion concentration (pH) upon the removal of the given pesticides from water by adsorption on activated carbon. Then, by utilizing a certain pH range, the effectiveness of activated carbon in removing given pesticides from water was determined.

Preparation of Activated Carbon

Two different activated carbons used in the determination of

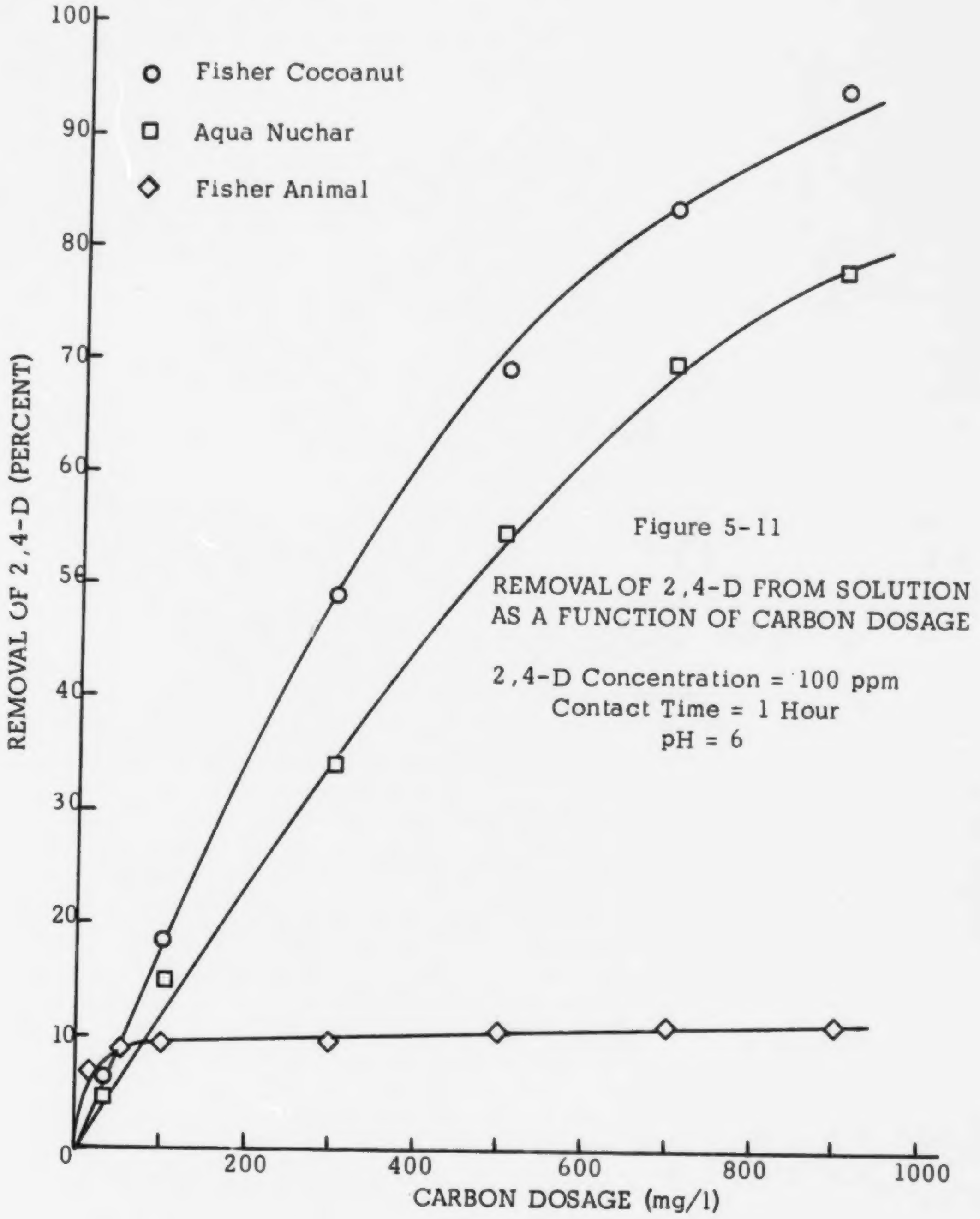


Figure 5-11

REMOVAL OF 2,4-D FROM SOLUTION AS A FUNCTION OF CARBON DOSAGE

2,4-D Concentration = 100 ppm
Contact Time = 1 Hour
pH = 6

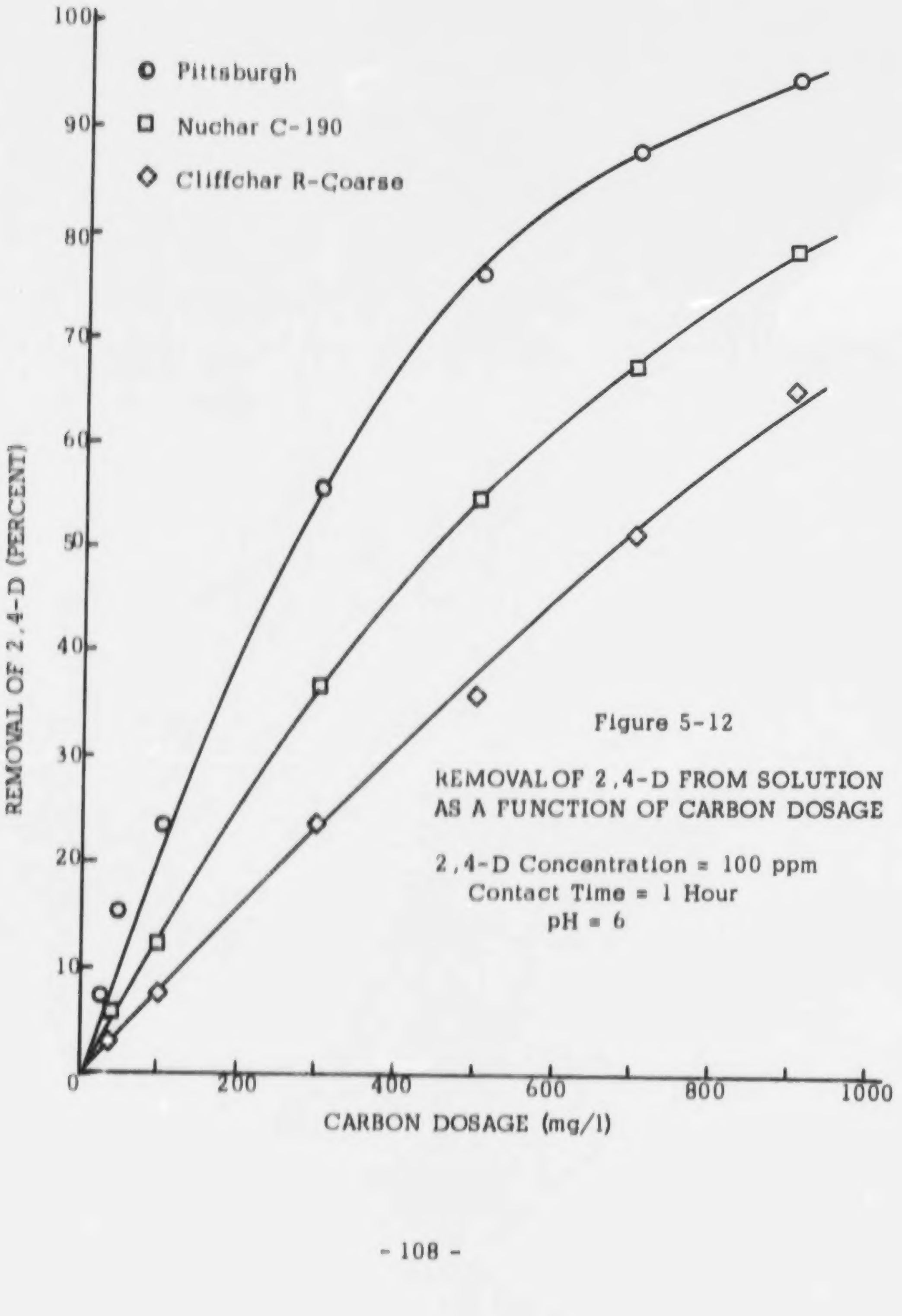


Figure 5-12

REMOVAL OF 2,4-D FROM SOLUTION AS A FUNCTION OF CARBON DOSAGE

2,4-D Concentration = 100 ppm
Contact Time = 1 Hour
pH = 6

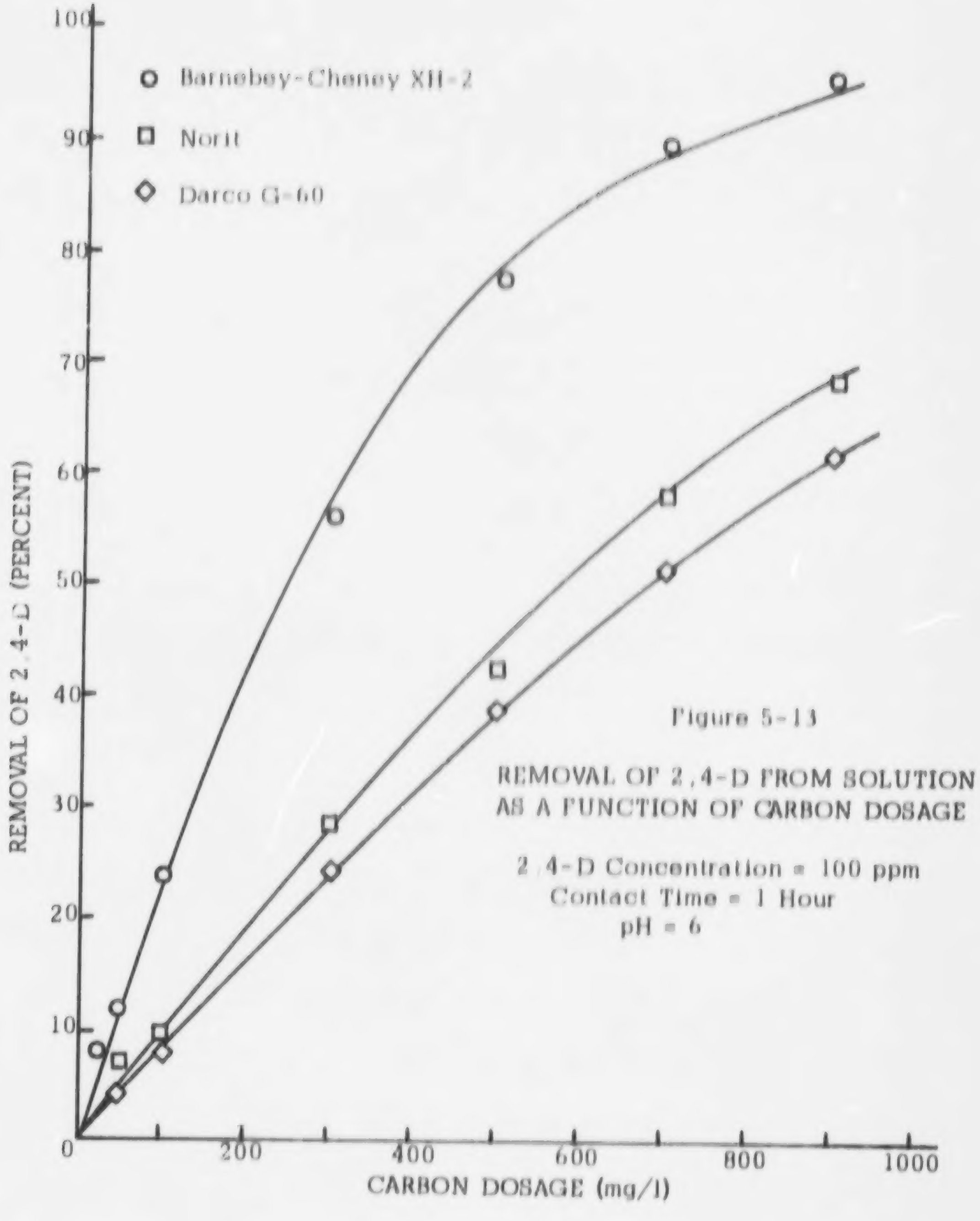


Figure 5-13

REMOVAL OF 2,4-D FROM SOLUTION AS A FUNCTION OF CARBON DOSAGE

2,4-D Concentration = 100 ppm
Contact Time = 1 Hour
pH = 6

the removal of the given pesticides from water. Barneby-Cheny XH-2, which is manufactured commercially from wood charcoal or lignite, was obtained from the Barneby-Cheney Company. Fisher Cocoanut, which is manufactured commercially from cocoanut shells, was obtained from the Fisher Chemical Company.

The preparation of each carbon consisted of crushing the carbon and separating out the particle sizes passing through a U. S. Standard Sieve number 140 and retained on a number 200; these particles were thus 0.089 millimeters in arithmetic mean diameter. Activated carbon of particle sizes as described above was used in removing the given pesticides from water.

Study of the Effect of pH Upon Carbon Adsorption

A study of the effect of pH on the removal of pesticides from water by activated carbon was determined by two experimental procedures. First, the change in count of the original mixture of each pesticide caused by varied pH values was determined. A 500 ml sample of each pesticide mixture was tested by placing the sample in a beaker which was placed on a magnetic stirring device. The pH values were varied from 10 to 1, and samples were taken as the pH value was reduced by the addition of acid. The changes which occurred in the concentration of pesticide as a result of these changes in pH are shown in Figure 5-14. A pH value of 6, the

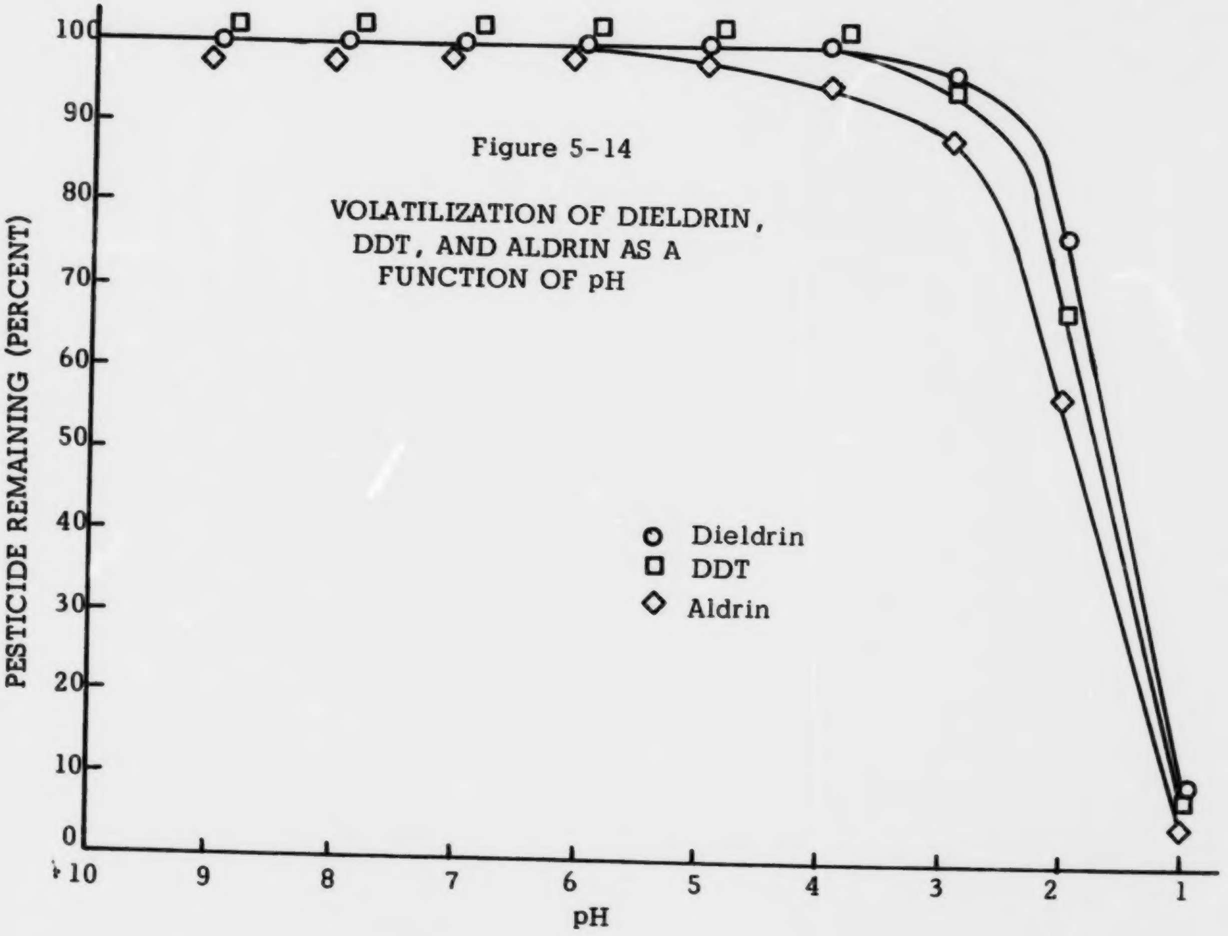


Figure 5-14

VOLATILIZATION OF DIELDRIN, DDT, AND ALDRIN AS A FUNCTION OF pH middle value of the pH range having a constant count, was used in subsequent tests.

Figure 5-14 illustrates the reduction in the concentration of the pesticides as the pH was lowered. The pesticides tended to remain in the water until a pH of approximately 3.5 to 3.0 was reached. Below a pH value of 3 the concentration of the pesticides in the mixture rapidly decreased. Secondly, the pH values were varied from 10 to 1 to determine the effect of the addition of activated carbon on the pH of the original mixture. A constant dosage of 20 mg of carbon in 200 ml of original mixture was placed in 250 ml flasks. The pH of the solution was varied from flask to flask and a duplicate of each test was performed to check previous results. After mixing the carbon and pesticide mixture for one hour, the mixtures were sampled and counted. The pH value of 6 was again determined to be the middle value of the constant count range (Figure 5-14). In this way, the pH value at which the pesticide concentration remained stable was obtained.

Another study was performed in which the pH of the mixture was varied and activated carbon was added to the mixture. The study was carried out over a pH range from 5 to 9, and in this range the pH did not seem to affect the removal of the pesticides from water by the carbon.

Study of the Effect of Contact Time of Carbon Adsorption

The purpose of this experiment was to determine the effect of time on the adsorption of the pesticides by activated carbon. The procedure consisted of placing 200 ml of pesticide mixture into a flask containing 60 mg of activated carbon (300 mg/l). Seven flasks, each containing 300 mg/l of carbon in a pesticide mixture, were then placed on a Burrell wrist action shaker and agitated for specified times of 15 minutes, 30 minutes, 45 minutes, 1 hour, 1.5 hours, 2 hours and 3 hours. At the specified time, a flask was removed and 125 ml. of the mixture was filtered through Whatman No. 42 filter paper. The filtrate was then sampled by placing five ml. of filtrate together with 15 ml. of scintillation liquid. The counts were observed and the necessary or optimum time needed for maximum removal of the pesticide from the mixture by the activated carbon was determined.

The rate of adsorption was extremely rapid during the first half hour of contact time after which the adsorption rate decreased as equilibrium between carbon and solution was approached. After one hour of contact time, the adsorption proceeded very slowly and was considered to be at equilibrium with respect to time. Weber and Morris (21) believe that the rapid initial rate of adsorption and the subsequent decreasing rate of adsorption is due to a rate-limiting-step which is controlled by the rate of diffusion of the solute particles into the capillary pores of the carbon.

The two carbons chosen for experimentation proved to be equally good adsorbents for the pesticides studied. Figures 5-15, 5-16, and 5-17 illustrate the percent removal for each pesticide for various contact times. The percent removal of DDT and aldrin varied almost linearly with the contact time up to seven or eight minutes at which time 50 percent of the pesticide had been removed. The percent removal of dieldrin varied linearly with the contact time for approximately six to ten minutes at which time 70 percent of dieldrin had been removed. The carbons had adsorbed 80 to 90 percent of each pesticide at 45 minutes and the remaining pesticide in solution was slowly adsorbed as time progressed.

Figure 5-18 illustrates another graphical method of representing removal of pesticides for given fixed carbon dosages and variable contact times. The concentration of the pesticide remaining in solution was plotted against the variable time. Four different dosages of carbon were used to demonstrate that the point of nearly maximum adsorption of pesticide occurred after approximately one hour of mixing.

Study of the Effect of Carbon Dosage Upon Removal of Aldrin, Dieldrin and DDT

The purpose of this experiment was to determine the effect of

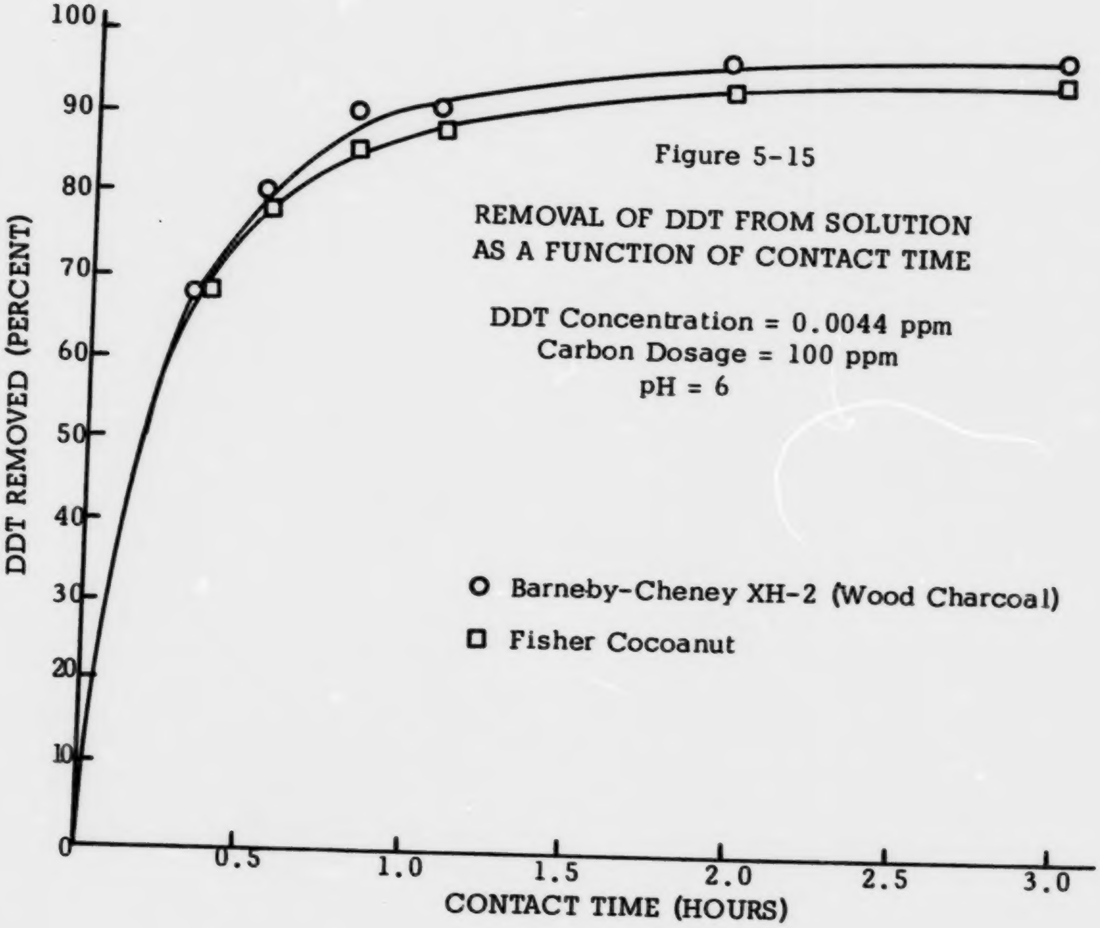


Figure 5-15

REMOVAL OF DDT FROM SOLUTION
AS A FUNCTION OF CONTACT TIME

DDT Concentration = 0.0044 ppm
Carbon Dosage = 100 ppm
pH = 6

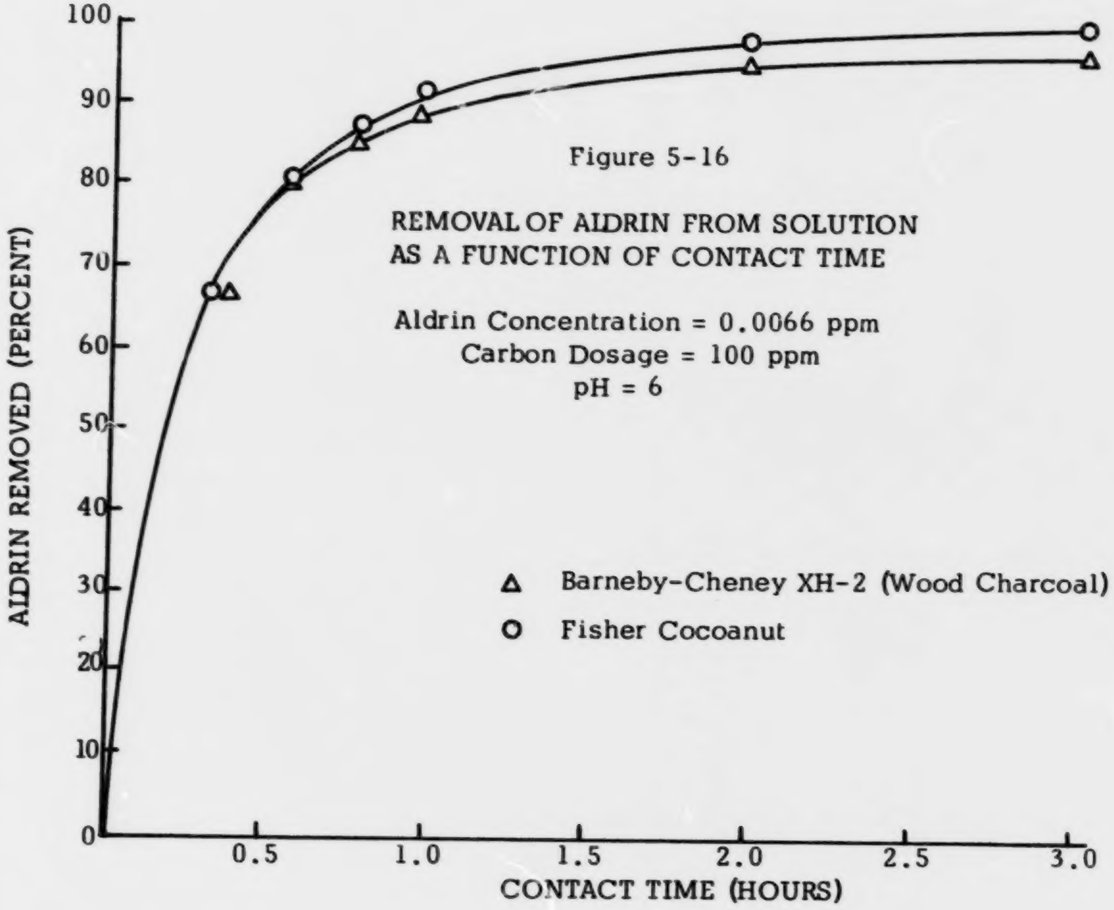


Figure 5-16

REMOVAL OF AIDRIN FROM SOLUTION
AS A FUNCTION OF CONTACT TIME

Aldrin Concentration = 0.0066 ppm
Carbon Dosage = 100 ppm
pH = 6

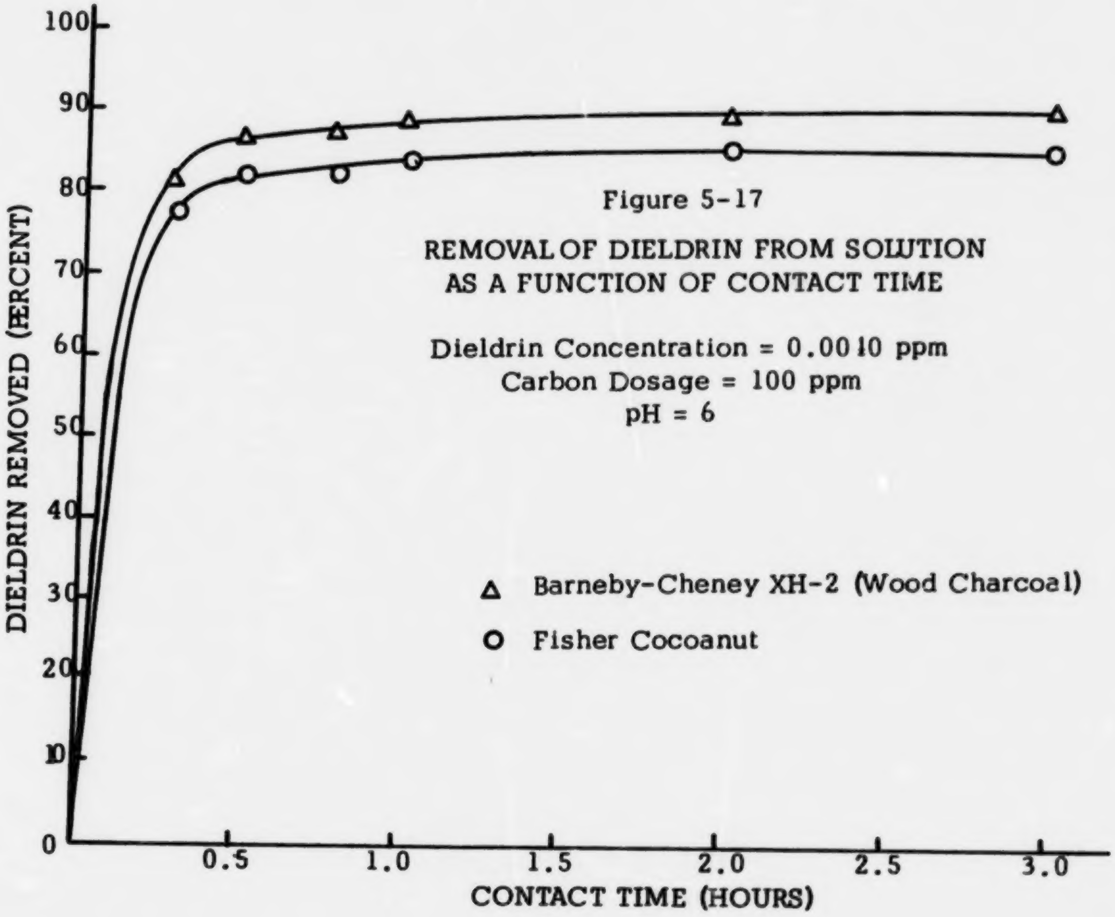


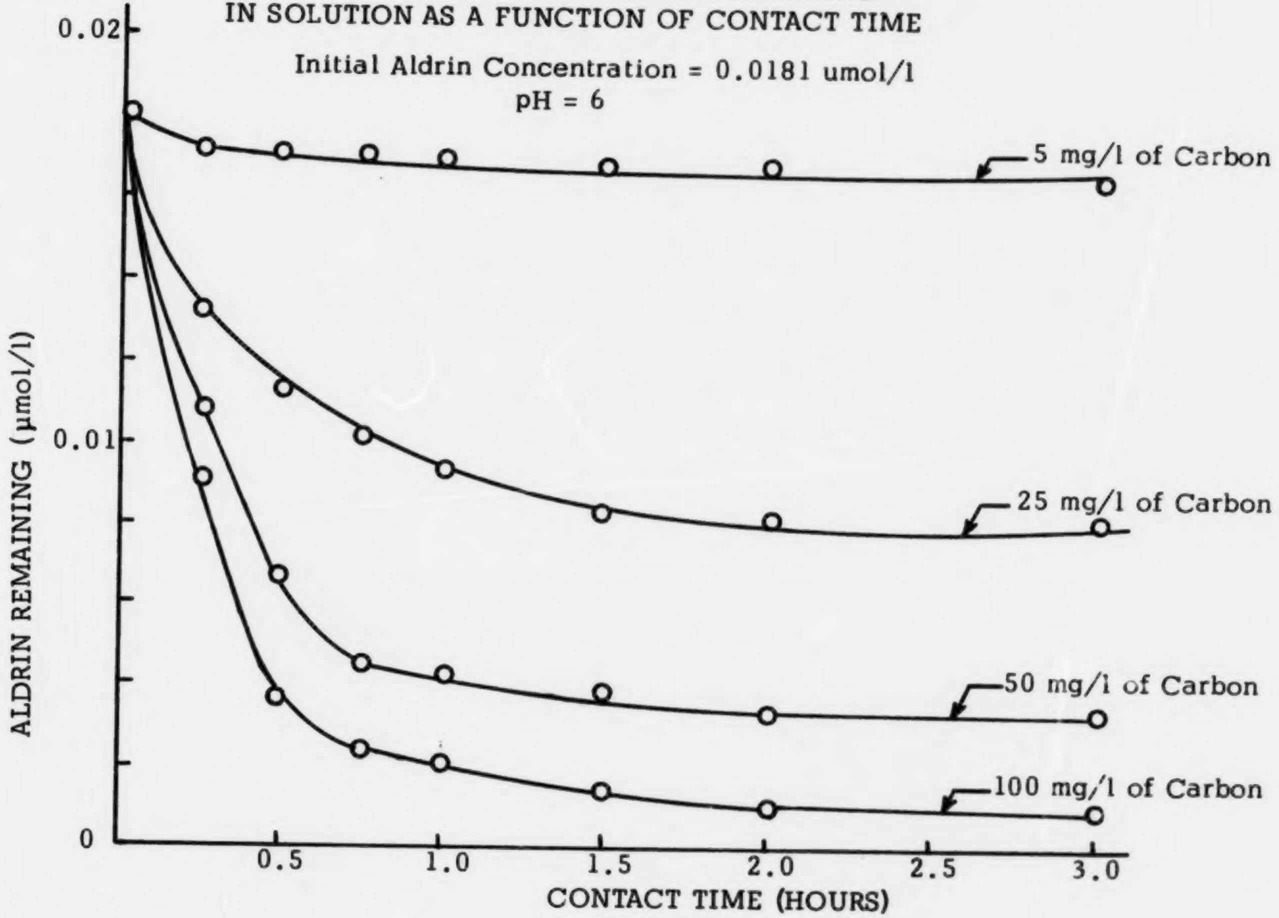
Figure 5-17

REMOVAL OF DIELDRIN FROM SOLUTION
AS A FUNCTION OF CONTACT TIME

Dieldrin Concentration = 0.0010 ppm
Carbon Dosage = 100 ppm
pH = 6

Figure 5-18

CONCENTRATION OF ALDRIN REMAINING
IN SOLUTION AS A FUNCTION OF CONTACT TIME


Initial Aldrin Concentration = 0.0181 umol/l
pH = 6

varied dosages of carbon on the adsorption of the pesticides with the time being held constant. The optimum contact time as previously determined was held constant for the test. The procedure consisted of placing 200 ml of pesticide mixture into a flask which contained a specific concentration of carbon (5 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, 300 mg/l, 500 mg/l, 700 mg/l, or 900 mg/l). The flasks were then placed on the shaker and mixed for the optimum time. After this time had elapsed, all flasks were taken from the shaker; and the carbon was filtered from the mixture. The filtrate was sampled and counted on the scintillation counter. All experiments were duplicated to check results. Figures 5-19, 5-20, and 5-21 illustrate the percent removal of pesticide for each carbon dosage. In each case, 100 mg/l of carbon removed 80 to 90 percent of the pesticide, and increasing dosages of carbon removed almost 100 percent of the pesticide.

EXPERIMENTAL STUDIES OF ADSORPTION ON CLAY

Studies With Aldrin, Dieldrin, DDT, 2,4-D BHC, Captan, and 2,4 5-T

The objective of the laboratory experimentation was to determine the effectiveness of clays in removing certain pesticides from water. Tests were conducted at room temperature. The first portion of the study was made using dieldrin, aldrin, 2,4-D, DDT and three types of clays. The tests were conducted using procedures similar to

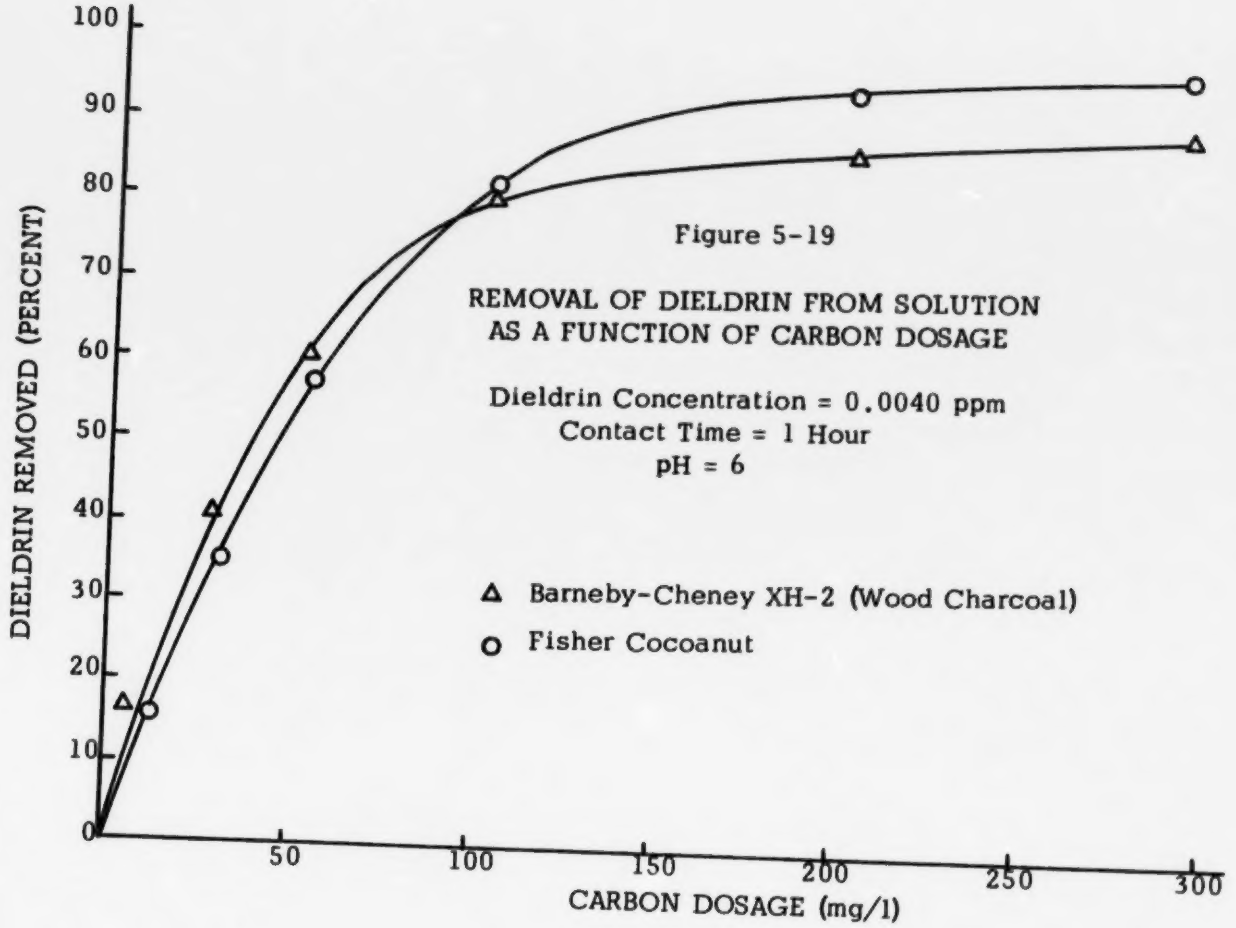


Figure 5-19

REMOVAL OF DIELDRIN FROM SOLUTION
AS A FUNCTION OF CARBON DOSAGE

Dieldrin Concentration = 0.0040 ppm
Contact Time = 1 Hour
pH = 6

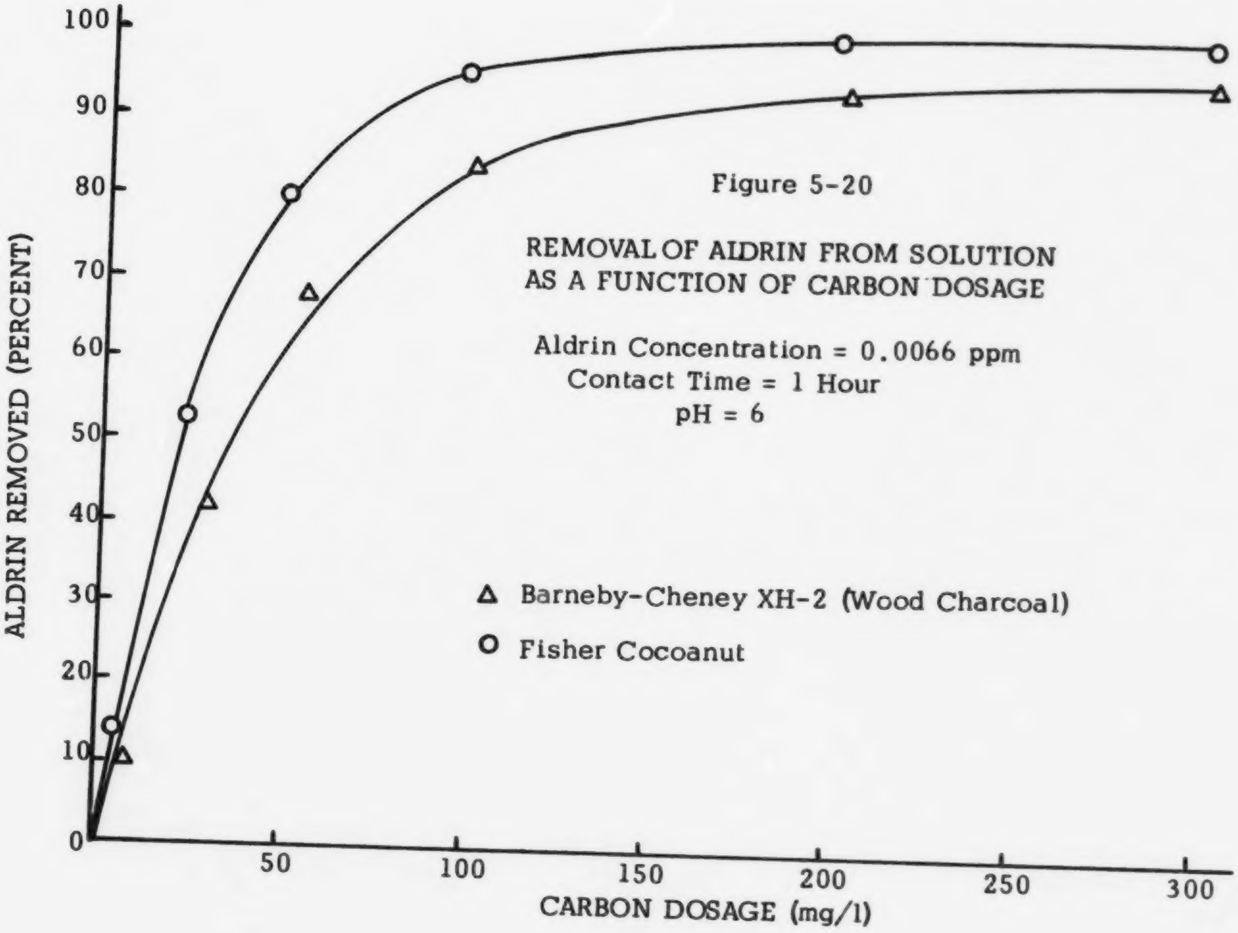


Figure 5-20

REMOVAL OF AIDRIN FROM SOLUTION
AS A FUNCTION OF CARBON DOSAGE

Aldrin Concentration = 0.0066 ppm
Contact Time = 1 Hour
pH = 6

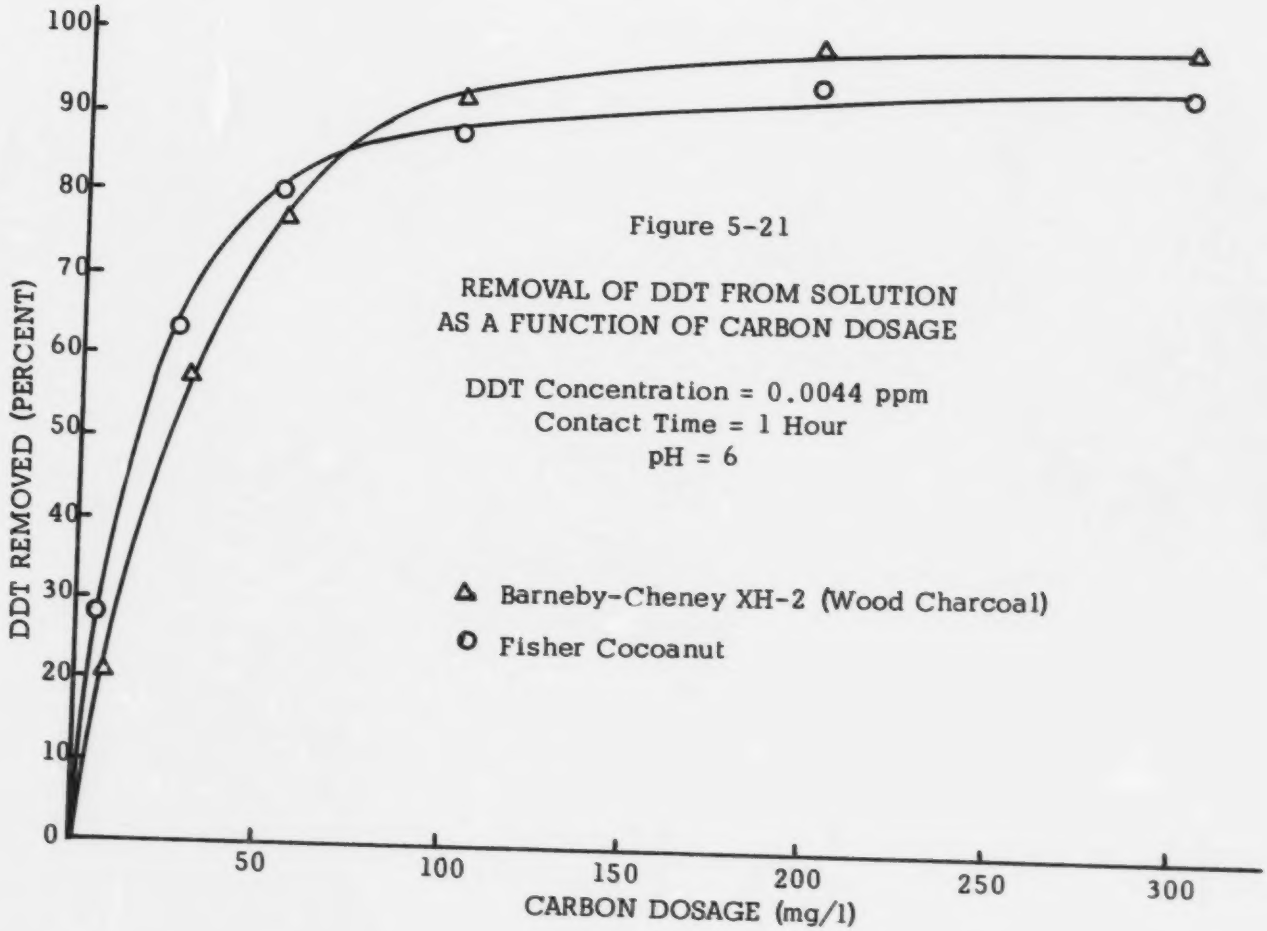


Figure 5-21

REMOVAL OF DDT FROM SOLUTION AS A FUNCTION OF CARBON DOSAGE

DDT Concentration = 0.0044 ppm
Contact Time = 1 Hour
pH = 6

those used for the carbon adsorption tests. The pesticide mixture with a dosage of 200 mg/l of clay was placed in a 250 ml flask on a Burrell wrist action shaker. Samples were collected at time intervals of 30 min., and 1, 2, 3, and 4 hours. The samples were filtered through 450 mμ filters to remove the suspended clay particles and then counted to determine the percent loss. The clays used in this study were: EPK - Edgar Plastic Kaolin, hydrous aluminum silicate obtained from the Edgar Plastic Kaolin Company, Edgar, Florida; Bentonite, U. S.P. obtained from the Fisher Scientific Company, Fairlawn, New Jersey; and Diluex, a hydrous magnesium aluminum silicate, obtained from the Floridin Company, St. Louis, Missouri. The pesticides used were aldrin, dieldrin, DDT, 2,4-D. Tests were completed with all combinations of pesticides and clays, and in no case was there any removal of pesticide from solution by adsorption on the clays.

The second portion of the study with clays consisted of providing a longer contact period between the clays and pesticide to determine if this was the limiting factor in the previous tests. In the field the contact time in many cases would be much greater than that provided in the first tests, and this was mainly the reason for the second portion of the tests. The test consisted of placing 2,000 ml of each of the six pesticides to be tested in separate one gallon bottles which were covered to prevent evaporation. These bottles were placed on magnetic stirrers and allowed to mix before the initial samples were gathered. After the initial samples were obtained, 500 mg of Diluex was placed in each of the six bottles to provide a dosage of 250 mg/l. Samples were collected at the end of 14 days and 20 days of mixing. The samples collected were centrifuged and the supernatant sampled and counted to determine the percent adsorption. The results of these tests are shown graphically in Figure 5-22 in which the percent removed is plotted as a function of time. At the end of twenty days 50 percent of the dieldrin and 25 percent of the DDT had been removed from the mixture by adsorption on the clay. The other pesticides tested showed a significantly lower adsorption on the clay.

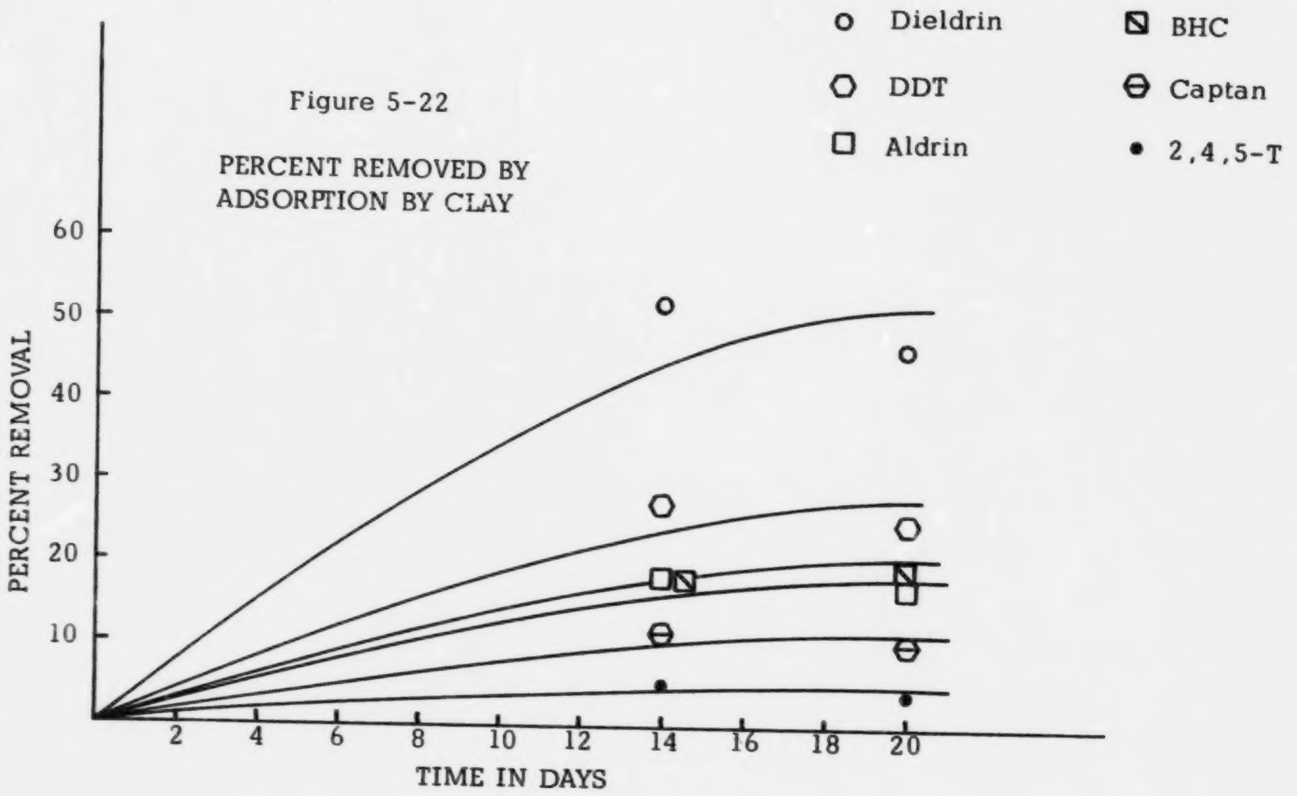


Figure 5-22

PERCENT REMOVED BY ADSORPTION BY CLAY

CHAPTER VI

THE REMOVAL OF PESTICIDES FROM WATER BY SURFACE ACTIVE AGENTS

There have been rather extensive studies on the removal of inorganic and organic materials from water by the foam fractionation process. Most of these have dealt with the use of this process as a means of treating domestic or industrial wastes. Hansen and Gotaas (29) applied flotation to sewage treatment some years ago in an attempt to remove suspended and colloidal solids from sewage. The process consists of buoying the sewage solids to the surface by means of air bubbles. A frothing or foaming agent was added to the sewage to facilitate the attachment of solids to air bubbles. The concentration of the flotation agent at the liquid-gas and solid interfaces promotes attachment of the particles to the air bubbles. These workers found lauryl amine hydrochloride extremely effective in reducing suspended solids by 95 to 99 percent, bacteria by 99 to 99.9 percent, and BOD by perhaps 50 to 80 percent. However, only 25 to 40 percent of the dissolved solids was removed. The cost of the additive was thought to be high and apparently the work was not continued.

I. A. Eldib (30) also applied the foam fractionation process to the removal of soluble organics from waste water. He first concentrated, isolated, and identified some of the organic material contained in a waste sample. Synthetic detergents, insecticides, o-nitrochlorobenzene, phenyl ether, phenolic compounds, petrochemical wastes, aliphatic and aromatic hydrocarbons and natural materials were found in this sample. A brief study was then made to determine if foam fractionation could be used to remove soluble organics from a secondary waste water effluent and the results indicated that these impurities could be removed by foam fractionation. Foam fractionation experiments were then carried out on a filtered secondary effluent. After foaming, the treated effluent was analyzed for alkyl benzene sulfonate (ABS) content and chemical oxygen demand (COD). Further tests on industrial waste effluents indicated that commercial dyes could be removed using this process but that phenol removal would be difficult.

Further tests along this same line were run by E. Rubin and R. Everett, Jr. (31). They concluded that activated sludge sewage plant effluents could be purified, at least partially, by foaming. Alkyl benzene sulfonate and other refractory organic compounds, measured by COD, could be removed.

For continuous-feed foaming of both filtered and unfiltered secondary effluent, a correlation existed between volume of air available per unit mass of ABS in the feed and the residual ABS concentration. Specifically, 1.5 liters of air per mg. of effluent ABS generally leaves a 0.4 mg/l residual concentration. This is significant because according to USPHS 1961 standards, the maximum allowable concentration in drinking water is 0.5 mg/l.

For unfiltered effluent, a relationship existed between percent COD removal and the dimensionless ratio obtained by multiplying the air-to-feed flow rate ratio by the COD-to-ABS concentration ratio in the feed. When the dimensionless ratio was 150, a maximum of about 40 percent COD removal was obtained. In the limited number of experiments where surface-inactive and/or surface-active substances were added, COD removal was either inferior to or at best comparable to that obtained without additives.

Experimental studies conducted by A. K. Sengupta and W. O. Pipes (32) were directed toward determining the effects of salts and low molecular weight organics on ABS removal utilizing the foam fractionation process. The data obtained from this investigation indicated clearly that some solutes have a pronounced effect upon the foaming of an ABS solution. Ionizable solutes, either organic or inorganic, increase foam production and foam stability when the total concentration of anions is less than 200 mg/l; however, at concentrations greater than 200 mg/l foaming is suppressed. Extremely water soluble organic compounds have very little effect upon foaming but water insoluble organic compounds suppress foaming completely at higher concentrations.

R. B. Grieves and R. K. Wood (33) made a study of the feasibility of using a foam fractionation process as a treatment process for aqueous refining and petrochemical wastes containing low concentrations of soluble organic compounds. They reviewed previous studies on the properties of foams and on the application of foaming to separation procedures and discussed the overall considerations involved in a foaming process. The foaming process studied by these authors involved adding detergents to raw water and bubbling air through the mixture to generate a foam. Insoluble impurities were concentrated in the foam and removed. They concluded that such an operation appeared quite economical, requiring only power for the compressed air, pumps for the liquid waste, and thermal or mechanical energy for foam collapse. The actual design and operation of a continuous foaming unit would depend not only on the desired separation but also on the properties of the waste and of the foam. Grieves and Wood are currently conducting research supported by the U. S. Public Health Service on the fundamentals of the foam fractionation process.

The foam fractionation process has also been used in the scientific field as a technique for separating protein and other biological materials. It has long been known that aqueous protein solutions possess appreciable foaming power and yield foams differing in composition from their bulk solutions. Some of the most recent work on the use of foam separations in the area of proteins is that by Gaden and Schnepf (34). In this work the effects of pH and concentration on the separations obtained by foaming aqueous solutions of two proteins, bovine serum albumin and glucose polymer dextran, were determined and found to be maximum at the isoelectric pH. At this point the protein exhibits highest surface activity with enrichment falling off with either increasing or decreasing pH. The enrichment ratio was also found to increase with decreasing bulk concentration. As expected, no enrichments were obtained for the dextran which exhibited no surface activity.

A selective method of removing and/or concentrating bacterial spores and vegetative cells from the culture growth medium by foam flotation was described by Boyles and Lincoln (35). Here, the authors do not distinguish between foam fractionation and froth flotation but combine both names and refer to the technique employed as foam flotation. Several factors which are important in the foam flotation process were investigated in this study. Spores from autolyzed cultures, _Bacillus_ _subtilis_ var. Niger and cells of _Serratia_ _narcescens_ were collected more effectively with fine rather than with coarser spargers. The effects of pH, sodium chloride, and genetic colonial type on collection of spores were studied as well.

Studies by Gaden and Kevorkian (36) showed that alcohol in water can be concentrated in the foam phase. Their data show that by the use of a stage process the alcohol can be removed completely from the water. It was also shown that in foaming solutions containing volatile compounds varying the degree of saturation of the inlet gas stream permitted a marked change in foam phase-residual liquid concentration relationships.

Studies have also been made to determine the feasibility of using the foam fractionation process as a means of removing metals from wastes. Work by Gaden et.al. (37) was directed toward removing from radioactive wastes such metal ions as strontium and cesium. Since solutions of these metal ions are not surface active, the foaming of such solutions should yield no separation. To use foaming techniques for the separation of metals the metallic ions must first be made surface active. This can be done by associating the metals in solution with some surface active material such as an anionic surface active agent, a chelating or complexing agent, or other negatively charged materials exhibiting surface activity. Solutions of varying strontium concentrations were foamed using Areskap 100 (a commercial anionic surfactant) as the foaming complexing agent. Enrichment in the foam was observed and the enrichment ratio increased quite rapidly with decreasing concentration of strontium.

Schoen, Rubin and Ghosh (38) ran a number of experiments to determine the feasibility of using the foam fractionation process as a means of removing radium from uranium mill wastewater. These experiments studied the effect of pH, radium concentration and foaming agent concentration on the removal. Their experimental results indicated that when the radium concentration was low and the foaming agent was present in a large excess, good enrichments of radium can be obtained. The pH had a considerable effect on radium enrichment but it was possible to find an effective foaming agent for practically every pH. The experimental evidence also indicated that the enrichment ratio was practically independent of radium concentration. Based on the test results it was concluded that foam separation would be an effective means of removing radium from dilute aqueous solutions.

Foam Fractionation

Foam fractionation is a process by which a solution containing a surface active solute is separated into two fractions, the foam fraction which has a higher concentration of the surface active solute than the original solution and a drain fraction depleted of surface active material (39). The method of effecting the separation is to produce a foam by vigorous aeration or agitation and then to separate the foam from the bulk of the solution by mechanical or other means (40). When the foam is initially produced, the surface active solute is preferentially adsorbed on the air water interfaces of the bubbles, and thus the foam is richer in surface active material than the residual bulk solution (41). The most popular quantitative description of this type of adsorption is given by the Gibbs adsorption isotherm (42).

Gibbs formulated an adsorption isotherm that relates the degree of adsorption at the boundary between two phases to the change in interfacial tension at that boundary and the composition of the two phases.

For an ideal, aqueous solution containing a single solute at equilibrium and constant temperature, the Gibbs equation is (42):

$$E_s = -\frac{x}{RT}\frac{d\gamma}{dx} = -\frac{1}{RT}\frac{d\gamma}{d\ln x}$$

where E_s = surface excess, g-moles/cm^2

x = bulk liquid solute concentration, g-moles/cm^3

R = universal gas constant, dyne cm/g-mole ^{o}K

T = absolute temperature, ^{o}K

γ = surface tension, dynes/cm

This equation indicates that the surface excess is determined by the rate of change of the surface tension and the change in the logarithm of the solute concentration. For very low concentrations this equation reduces to:

$$E_s = \frac{kx}{RT}$$

where k is a constant.

If the Gibb's isotherm is to hold true for the pesticides which are normally surface inactive products the materials must be first made surface active by the addition of a "collector," which is a surface active agent which has the ability to attract the surface inactive component (39). One method of doing this would be to take advantage of the principle of attraction between ions of opposite charge. A surfactant ion of charge opposite to the ion to be removed is added to the solution and reacts with the inorganic ion to form an insoluble soap which may then be carried to the surface with the foam. If this process is to be effective, the collector must be introduced in such a way that it exists as simple ions; and the inorganic material must have an ionic charge (39).

A second way utilizes the relationship between solubility and surface activity. Solubility results from a molecule collecting in regions of the solution where it is most surrounded by the solvent liquid whereas surface activity results from the molecules being least surrounded (39). In order for a successful separation of soluble organics from water to take place, it may be necessary to reduce the solubility of these organic compounds. In some cases this may be done by reducing the temperature at which the foaming takes place, or by altering the pH if this has an effect on the solubility (39). Under conditions of minimum solubility, the decrease of surface tension of the water would be large and foam fractionation would be expected to be more effective. The collector could combine chemically with the organic compounds and remove them in the foaming process. If the compounds are nonwettable they are transported to the liquid surface by air bubbles where they become trapped in the foam and are removed.

Successful foam fractionation depends on the nature of the foam as well as the adsorptive characteristics of the system. In this connection, two of the more important properties of foams are stability and drainability (43,44). Drainability is the property that permits liquid to flow from the lamellae separating individual gas bubbles when acted upon by gravity and suction at Plateau's borders. (The "Plateau's border" is the small triangular column formed when the septums of three bubbles are joined together (44).) Stability is the property that enables foams to withstand the lamellar thinning which results from drainage without rupturing (44).

Foam stability requires (a) that the concentration of the surface layer be different from that of the bulk liquid, and (b) that the surface layer have an abnormally high surface viscosity. Some of the important factors affecting foam stability are bulk solute concentration, pH temperature, and bubble diameter (43,44). Maximum foam stability occurs at the critical concentration for micelle formation. In general, the foaminess of aqueous solutions of inorganic compounds is low compared to that of aqueous solutions of many alcohols, organic acids, bases, and salts. Low concentrations of ionizable solutes increase the foam rate and, by inference, the foam stability (44).

The size of the bubble also has an effect on the stability of the foam. From free surface energy considerations it can be shown that films of large surface area are less stable than those of small area because they require a large force in the film to oppose the external forces. Therefore, the smaller bubble is more stable because it requires less elastic surface force to resist rupture (44).

Foam drainage is a thinning of foam lamellae without rupture, but the usual methods for determining drainage cannot differentiate between liquid originating from unbroken lamellae and that yielded by ruptured films. The liquid in the foam drains because of (a) gravity and (b) suction by Plateau's border (44).

Very little is known about the relation between the persistence of a foam and its rate of drainage. Little experimental information is available to describe the rate of drainage of simple systems, such as aqueous alcohols, because the lifetime of the foam is too short. It is known, however, that if the bubble diameter is small the drainage will be poor and that if this "small bubble" foam is long lasting a large amount of liquid will be trapped and removed from the solution. The drainage of foams is naturally affected by the viscosity of the draining liquid; the higher its viscosity, the lower its drainage rate. Thus, an increase in temperature will cause a decrease in viscosity and an increased drainage rate, but at the same time may make the foam more unstable (43,44).

In some cases, small amounts of polar organic compounds may markedly lower the drainage rate of detergent foams. This effect can be made to disappear by heating the system. This takes place over a narrow range of temperature, generally of the order of 2°C or less, termed the "drainage transition temperature." This transition is dependent only on the composition of the solution with which the foam is in equilibrium, and is independent of the distribution of bubble size or of the particular conditions in the foam.

These phenomena are not yet understood satisfactorily (43,44).

The removal of non-surface active materials from a solution by foam fractionation can be greatly affected by two important operational variables. The two operation variables are collector concentration and refluxing enrichment. The collector concentration, usually reported as the ratio of the collector concentration to the non-surface active material concentration, greatly affects the removal of the non-surface active material from the solution. For a continuous predetermined percent removal of the non-surface active material by the collector, this collector ratio must remain constant. An increase in the non-surface active material concentration would increase the amount of collector required for the same percent removal. This indicates that the ultimate removal of the non-surface active material by foam fractionation is a direct function of the collector ratio and not the non-surface active material ion or collector concentrations (39).

The second variable is the foam refluxing enrichment process. When solutions containing surface active solutes that have attached themselves to non-surface active materials are foamed, the foam becomes enriched with these solutes and the residual bulk liquid is depleted. If the enriched foam is not removed but broken and allowed to drain back into the residual bulk liquid further enrichment will take place as the solution is foamed again. This procedure can be repeated a number of times with each time increasing the removal until the desired removal is obtained. Then the foam is removed from the foaming apparatus, collected and collapsed to produce a solute-rich liquid product which can be disposed of easily.

Laboratory Investigations

The purpose of this investigation was to study the effectiveness of several surface active agents in removing pesticides from water. The chlorinated hydrocarbon pesticides aldrin and dieldrin were the ones whose removal was studied in this investigation.

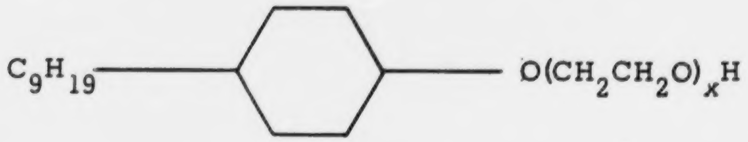
In the first portion of the investigation, the effect of hydrogen ion concentration (pH) upon the removal of the pesticides from solution by surface active agents was studied. The second portion of the investigation involved determining the effect of surface active agent dosage on the removal. The third portion of the study was directed toward determining the effect of reflux time on the removal. The final part of the investigation was directed toward determining the effect of repeated dosing upon a single solution sample.

Selection of Surface Active Agents

Three surface active agents, alkyl benzene sulfonate (anionic), Dowfax 9N9 (nonionic), and Aerosol C-61 (cationic) were selected for use in this study. They were selected primarily for their ability to generate good, stable foams at fairly low dosages. They also had to be non-volatile, contain a high percent of active ingredients by weight and have a pH of 6.0 or greater.

Until recently, alkyl benzene sulfonate was the most widely used surfactant on the market. The ABS selected contained 49.3% alkyl benzene sulfonate, 35.7% Na_2SO_4, 0.6% free oil, 2.4% NaOH, 5.4% Na_2Co_3, and 6.6% H_2O. The ABS was in a powdered form and required no special storage facilities.

The Dowfax 9N series of surfactants are condensation products of nonylphenol and ethylene oxide. Their structure can be represented as:



The number following the letter N in the product name indicates the approximate average number of moles of ethylene oxide condensed per mole of nonylphenol. Dowfax 9N9 was the one selected for this study and contained 100% active ingredients.

Surfactants derive their surface active properties from a hydrophobic-hydrophilic structure. In the Dowfax 9N products, the nonylphenol portion of the molecule functions as the water-insoluble or hydrophobic constituent, while the polyoxethylene chain imparts the water-soluble or hydrophilic character.

Aerosol C-61 is a mixture of the octadecyl amine and octadecyl guanidine salts formed by the reaction of octadecyl carbamic acid with ethylene oxide. It contains approximately 70% active ingredient in isopropyl alcohol and water. Its appearance varies from a soft tan paste to a clear brown liquid, depending upon temperature. It is stable in acid, alkaline, or neutral solutions. Aerosol C-61 is a good dispersing agent, and in low concentrations acts as a setting agent.

The physical and chemical properties of these surface active agents are listed in Table 6-1.

Selection of Aeration Rates

The aeration rate was not a test variable. After studying a number of references and performing a few tests, it was found that any air flow rate equal to or greater than 200 ml/min. would give a maximum removal of the surface active agent from the solution so it was decided to use a minimum air rate of 200 ml/minute.

Two other variables were also considered in selecting the air flow rate. It was found that the nature of the agent and the size of the bubble must be considered. Tests were run to determine what

TABLE 6-1

PHYSICAL AND CHEMICAL PROPERTIES OF THE SURFACTANTS

PROPERTY	ABS	DOWFAX 9N9	AEROSOL C-61
Ionic Nature pH, 1% aqueous solution at 25°C	Anionic 10.5	Nonionic 6.4	Cationic -
Active ingredient % by weight	49.3	100	70
Equiv. Weight	348	-	-
Cloud Point (1% Aqueous solution)	-	54°C	-
Specific Gravity 25°C	-	1.056	1.00
Solubility in water	-	10 weight percent	1% slightly turbid 5% viscous dispersion
Freezing point °C	-	1	-
Flash point	-	560°F	Approx. 80°C
Surface tension (dynes/cm)	-	31.8	34.3
Interfacial tension (dynes/cm)	-	2.9	6.5
Viscosity cks. at 25°C	-	238	-

air rate was required to cause the foaming of the agent to take place and to determine what air rate would give a desired bubble size.

After examining the results of the tests mentioned above, it was decided that the following flow rates of air would be used at standard temperature and pressure.

300 ml/min. for ABS

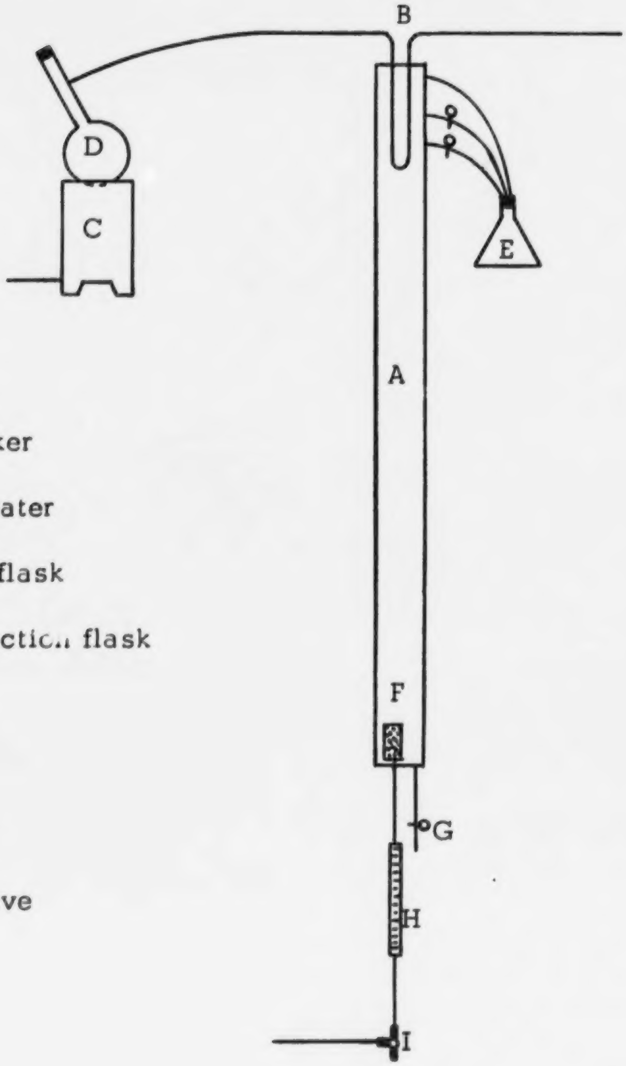
300 ml/min. for Aerosol C-61

200 ml/min. for Dowfax 9N9

These air flow rates generated good stable foams and were used for all tests conducted in this study.

Experimental Apparatus

A schematic diagram of the experimental apparatus is shown in Figure 6-1. The column consisted of a 1.00-inch ID glass tube about 48 inches in length. Three 0.25-inch diameter holes were drilled in one side near the top of the column, and short lengths of 0.25-inch ID glass tubing were fused to the column at these locations. Flexible polyvinyl tubing was used to connect these short protruding glass tubes to the foam collection flask. The bottom outlet was located 36 inches from the bottom of the column, the middle one 4 inches above the first and the top outlet 6 inches above the second. These openings were closed with pinch clamps except for the one being used to remove foam during a test. The particular outlet open



A. Column

B. Foam Breaker

C. Electric heater

D. Distilling flask

E. Foam collection flask

F. Air stone

G. Drain

H. Flowmeter

I. Needle valve

Figure 6-1

EXPERIMENTAL APPARATUS

depended on the surface active agent dosage, reflux time and foam height at various times in the test. The compressed air used in the foam fractionation process came from a laboratory supply line. The air flow was metered by a flowmeter and controlled by a needle valve. The air was introduced into the test apparatus through a porous air stone located at the bottom of the test column which evenly distributed the air throughout the tube cross section.

Test solutions were poured into the column through the open top and removed through a drain in the bottom. While the tests were running, the drain was closed with a pinch clamp; and the top was closed with either a plain rubber stopper or a rubber stopper containing a U-tube, depending on whether or not the refluxing procedure was being used.

If the refluxing process was being used, the U-tube was extended downward in the column until it was at least 1 inch below the bottommost foam outlet. Steam from a distillation flask was circulated through this U-tube and the heat produced by the steam in the U-tube broke the foam on contact without destroying the foaming properties of the surfactants.

Study of the Effect of pH

Preliminary investigation showed that a greater removal of aldrin and dieldrin was accomplished by the surface active agents at low pH values. This led to a study of the effect of pH on the pesticide in solution without any surface active agents being added. This study was performed by placing 500 ml. of the pesticide solution in a beaker on a magnetic stirrer. The stirrer was used to provide quick and complete mixing. The pH of the solution was adjusted in increments from 10.0 to 1.0. After being adjusted to each incremental pH value, the solution was allowed to stir for 15 minutes before being sampled. From this investigation, a range of pH values (4.0 to 10.0) was determined over which the pH had no effect on the pesticide in solution, and this range was used in subsequent tests.

Tests were then run to determine what effect the pH has on the removal of the pesticides from the solution by the surface active agents. These tests were performed by placing 5 mg. of the agent in a beaker containing 500 ml. of the pesticide solution. The pH of the solution in each beaker was adjusted prior to contact with the surface active agent, and a five milliliter sample was taken. The pH values for this test ranged from 10.0 to 4.0, and four different values were tested. This solution was placed in the test apparatus, and the foam fractionation process was carried out. Samples of the collected foam and the depleted solution were taken and counted and the amount of pesticide removed was determined. Duplicate tests were run to check the results and tests were also run for each surface active agent on each pesticidal solution.

Study of the Effect of Surface Active Agents Dosage Upon Pesticide Removal

The effect of surface active agent dosage was studied in much the same manner as that described in the preceeding section except that variable dosages of each surfactant were used instead of a varying pH. Surfactant dosages of 1, 2.5, 5, 7.5, 10, 20, 25 30, and 40 mg/l active ingredients were used. As before, 500 ml. solution samples were used in the test process. This solution was sampled and then dosed with the surface active agent. The mixture was then stirred and poured into the test apparatus. Air was bubbled through the apparatus at a rate of 200 ml/min. or 300 ml/min. depending upon the agent, and the resulting foam was collected. The test solution was then removed from the test apparatus and sampled. The collected foam was collapsed, measured for total volume, and then sampled. The samples were then counted and compared to determine the amount of removal.

This procedure was repeated for all the dosages and the resulting data was studied to determine the effect of surfactant dosage upon the pesticide removal. Duplicate tests were run to check the results and curves of removal as a function of dosage were plotted.

Study of the Effect of Reflux Time Upon the Pesticide Removal

This study was conducted in much the same manner as that described in the preceding section. The same dosages were used along with the same solution sample sizes. The mixture was placed in the test apparatus and aerated but the foam was not allowed to escape for a period of time. The foam was broken and the agent was allowed to drain back into the bulk liquid where it was further enriched. The reflux times used in this study were 0, 15, 30, 60, 90, and 120 minutes. After the predetermined reflux time had passed the foam was allowed to escape the apparatus to a collection flask where it was collapsed, measured for total volume and sampled. At the completion of the foaming stage, the bulk liquid was removed from the test apparatus and sampled. The samples were then counted and compared to determine the amount of pesticide removal.

This procedure was repeated for all agent dosages and for both pesticides, and duplicate tests were run to further check the results. The resulting data was studied to determine the effect of reflux time upon the pesticide removal, and curves of removal as a function of reflux time were plotted.

Study of the Effect of Repeated Dosing Upon the Pesticide Removal

This portion of the investigation was directed toward determining the effect of repeated dosing upon a single solution sample. The procedure was the same as that used in the previous studies. The optimum pH of between 6.5 and 7.5 and reflux time of one hour as determined by the previous studies were used for all tests. The dosage used depended on the foaming nature of the surface active agent and was usually the smallest dosage that would give a good stable foam. The sampling technique and removal calculations were the same as those used in the previous tests; but after the first test run, the stock solution was not destroyed. Instead it was dosed, placed in a clean apparatus, refluxed for one hour, foamed and then sampled again. This procedure was repeated for a varying number of times, the number depending on the surface active agent used and the pesticide in the stock solution. Calculations were then made, and by comparing the results for each pesticide with results from previous tests the effect of repeated dosing upon the pesticide removal was determined.

Experimental Results

Study of the Threshold Foaming Dosage

Studies were made to determine the effective foaming dosages for the surface reactive agents. The effective foaming dosage is the smallest surfactant dosage that will generate a good stable foam. These threshold dosages are important because even though a small dose of the surfactant might react with the pesticide, no removal could be effected unless enough of the surface reactive agents was present to generate a foam. Test results indicated that the effective dosages for the surfactants were as follows:

1 mg/l for Dowfax 9N9
2.5 mg/l for ABS
1.75 mg/l for Aersol C-61

These dosages are based on the active ingredients of the surfactants.

Study of the Effect of pH

Preliminary investigations showed that a greater removal of aldrin and dieldrin was accomplished by the surface active agents at pH values below 4.0. Studies were performed to determine the effect of the pH of the solvent on the pesticide in solution. These studies showed that above pH 4.0 the aldrin or dieldrin in solution were not affected while below pH 4.0, the pesticide remaining decreased approximately as a linear function of the decreasing pH. Less than 20 percent of the dieldrin was remaining in the solution at pH 1.0 while 90 percent remained in solution at pH 3.0. The aldrin was somewhat more stable. At pH 1.0, 42 percent of the aldrin remained while at pH 3.0, 96 percent remained. The results of this study indicated that lowering the pH of the solvent caused some change in the pesticide which made it become volatile. The volatilization of the pesticides as a function of decreasing pH is shown in Figure 6-2.

A study was also made to determine the effect of pH on the removal of aldrin or dieldrin from solution by surface active agents. A constant dosage of surface active agent was added to 500 ml. samples of 0.02 mg/l aldrin or 0.035 mg/l dieldrin solutions, and the pH of each solution was varied from 10.0 to 4.0. The results of this study are shown in Figures 6-3 and 6-4 where the percent pesticide removed is plotted against the pH of the solution. These curves show that in all cases a lowering of the pH increased the pesticide removal. It should be noticed, however, that this increase is much larger in the aldrin tests than in the dieldrin tests. Thus, it should be concluded that lowering the pH of the solution increased the removal of the pesticides by surface active agents but that the amount or rate of increase depends on the nature of the pesticide.

Study of the Effect of Surface Active Agent Dosage Upon Pesticide Removal

In this study, increasing doses of surface active agents were used to remove pesticides from solution. Since the pH tests indicated that there was very little differences in the percent removals from pH 6.0 to 8.0 it was decided to run all tests in this pH range. This is a pH range that would normally be encountered in a treatment

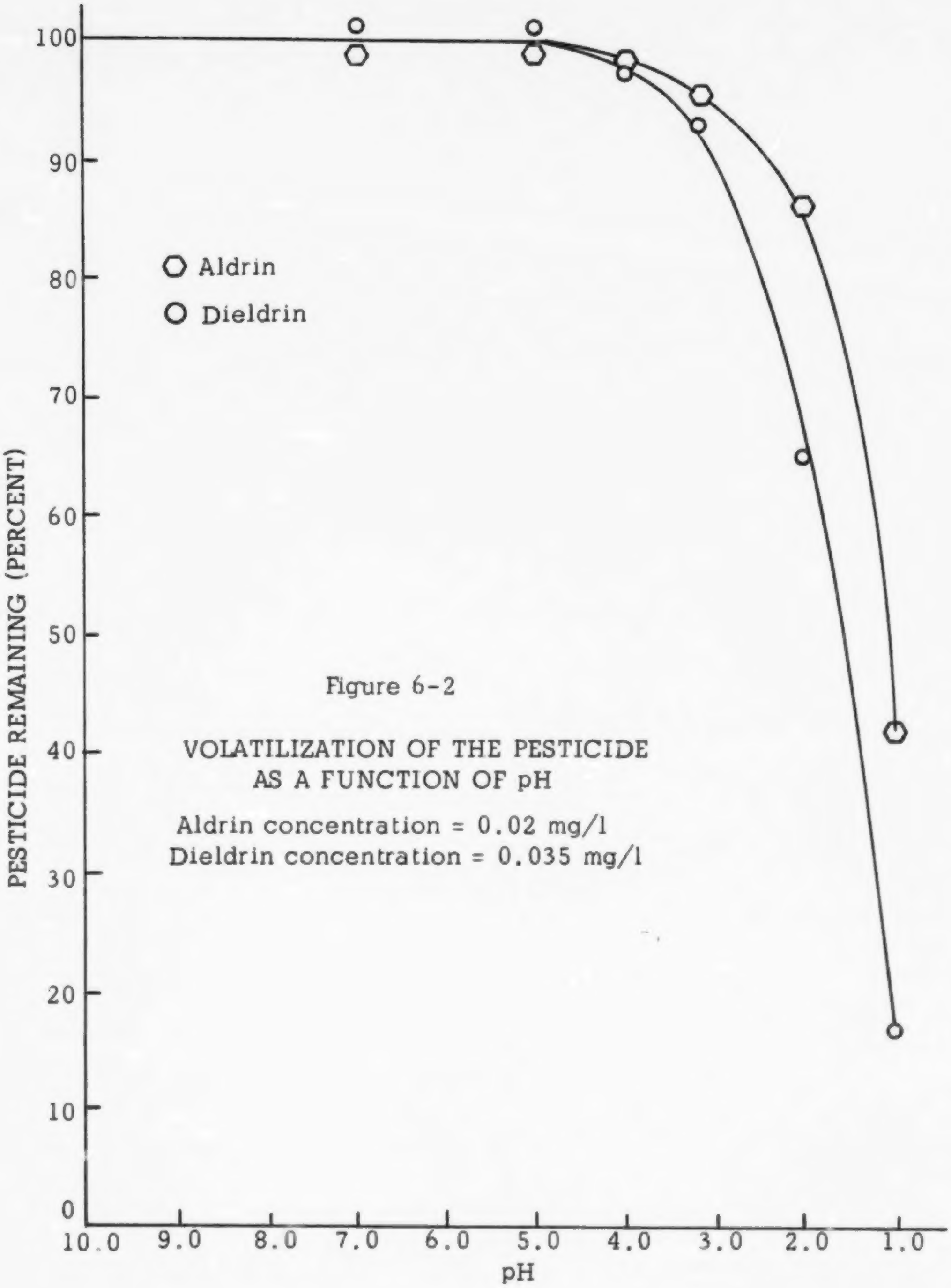


Figure 6-2

VOLATILIZATION OF THE PESTICIDE AS A FUNCTION OF pH

Aldrin concentration = 0.02 mg/l
Dieldrin concentration = 0.035 mg/l

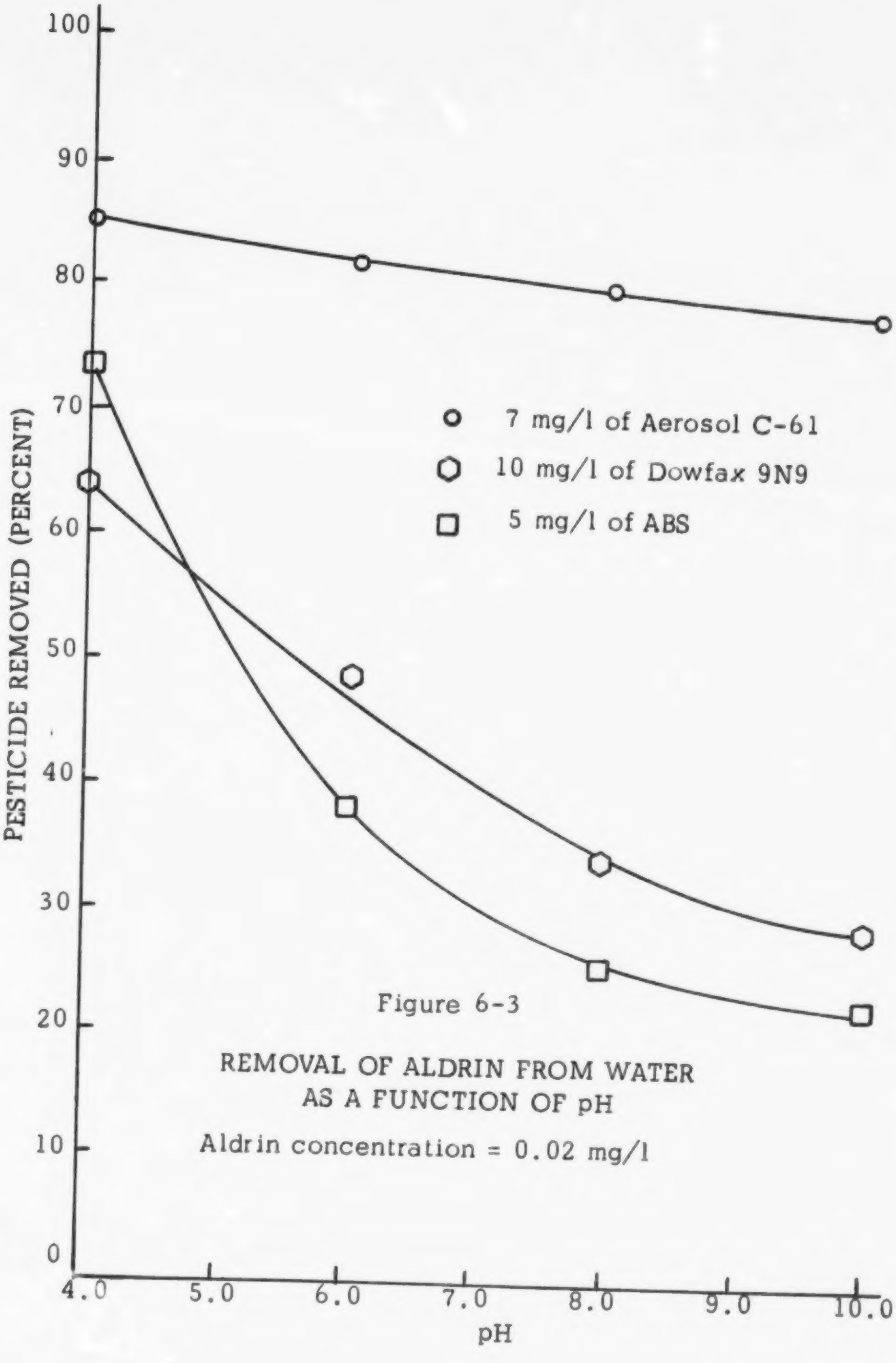


Figure 6-3

REMOVAL OF ALDRIN FROM WATER AS A FUNCTION OF pH

Aldrin concentration = 0.02 mg/l

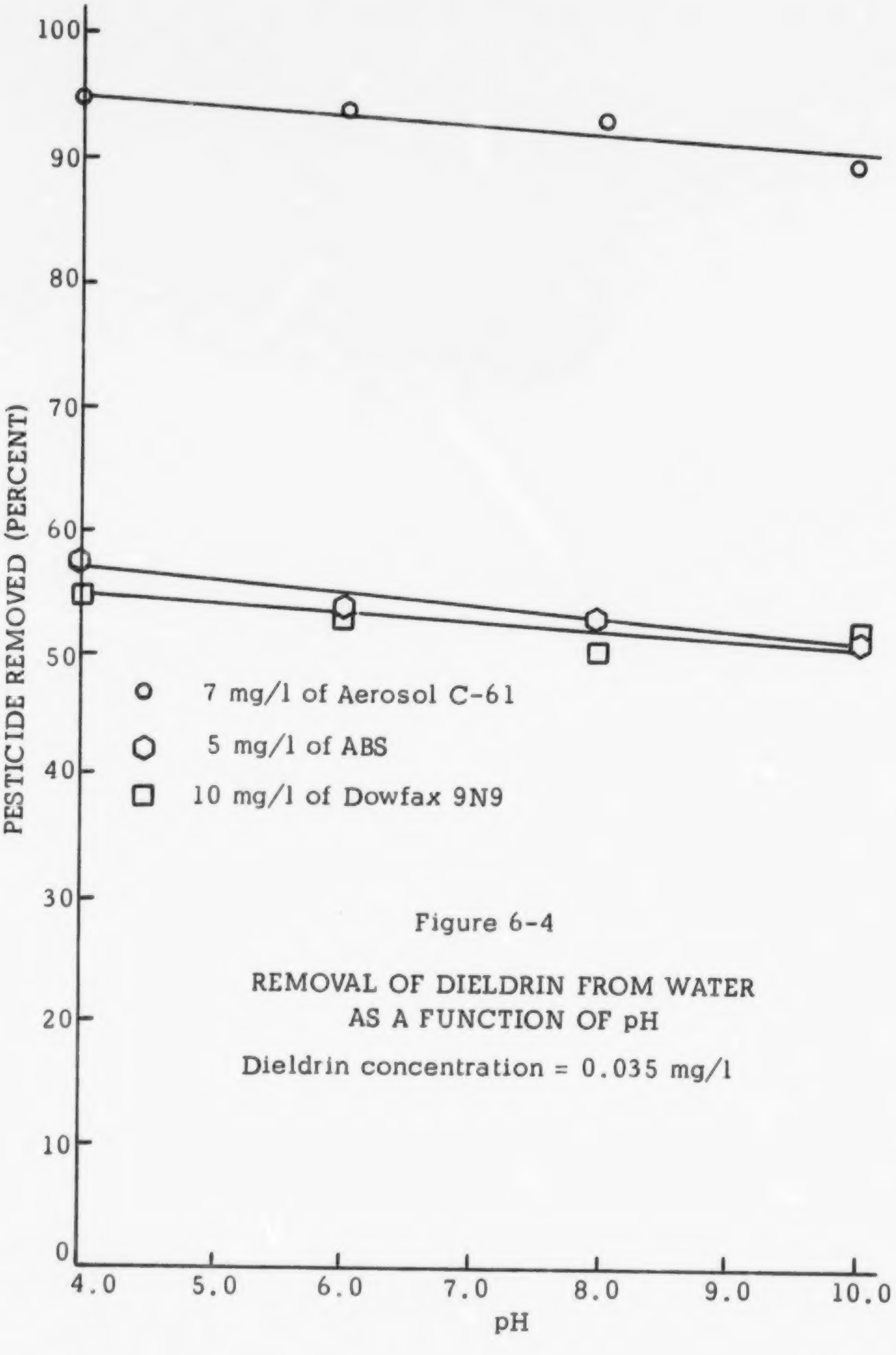


Figure 6-4

REMOVAL OF DIELDRIN FROM WATER AS A FUNCTION OF pH

Dieldrin concentration = 0.035 mg/l

facility and the stock solutions of aldrin and dieldrin had pH values that naturally were within this range.

The contact or foaming time for this study depended upon the nature of the surface active agent. Foaming times of one hour for Dowfax 9N9, one and one half hours for ABS and one hour for Aerosol C-61 were used. Figures 6-5 and 6-6 show the percent pesticide removed as a function of surface active agent dosage.

It should be noted that the percent removal rate increases rapidly as the lower dosages are increased but tends to level off at the larger dosages. All the surface active agents produced some removal but with both the dieldrin solution and the aldrin solution, a much higher percent removal was produced with the cationic agent (Aerosol C-61). It appears that aldrin and dieldrin carry a negative charge and that the large percent removal is due to charged ion attraction during the foam fractionation process. The substantial removal, as high as 60 percent, brought about by the anionic (ABS) and nonionic (Dowfax 9N9) agents could be due to either a chemical attachment of the pesticides to the surface active material or to a reduction in the solubility of the pesticide. If the pesticide becomes insoluble and nonwettable, it will be transported to the surface by the air bubbles and removed in the foam.

These results indicate that all three types of surface active

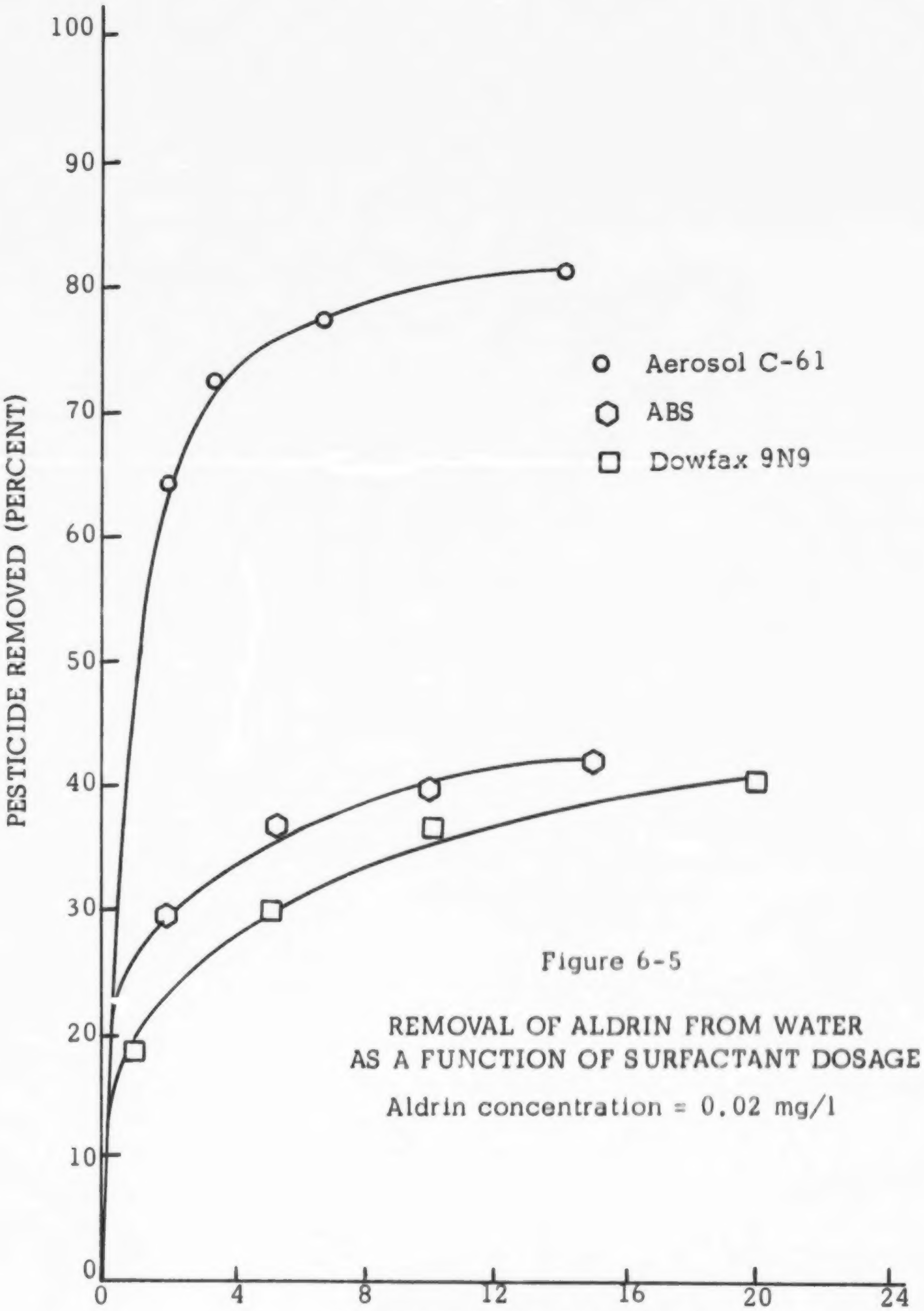


Figure 6-5

REMOVAL OF ALDRIN FROM WATER AS A FUNCTION OF SURFACTANT DOSAGE

Aldrin concentration = 0.02 mg/l

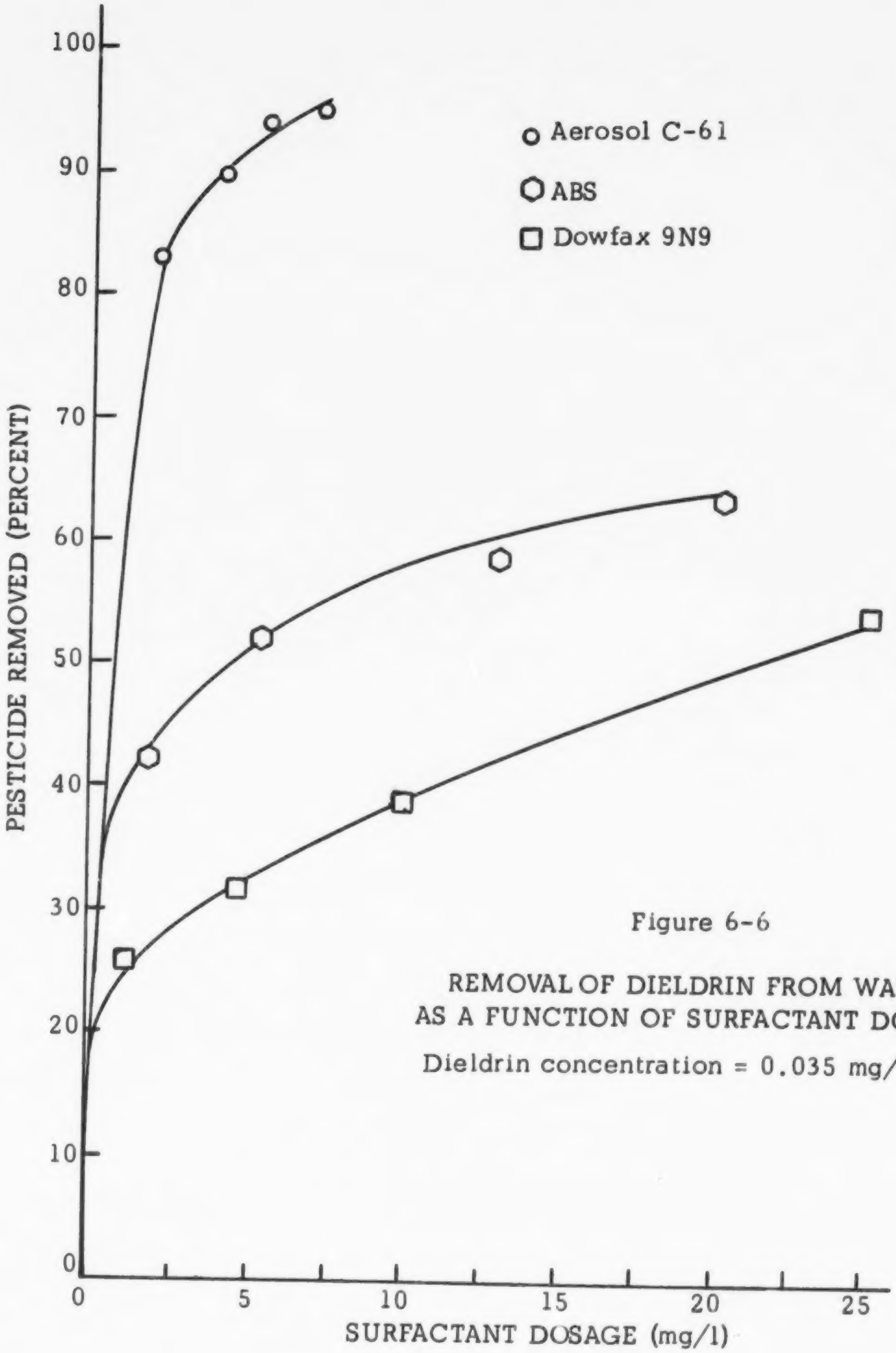


Figure 6-6

REMOVAL OF DIELDRIN FROM WATER AS A FUNCTION OF SURFACTANT DOSAGE

Dieldrin concentration = 0.035 mg/l

agents will remove the pesticides from water but the best results appear to be due to a charged ion attraction. If the pesticide does not carry an ionic charge, then any of the agents will produce some removal but a large dosage will be needed.

Study of the Effect of Reflux Time Upon the Pesticide Removal

In this investigation a reflux procedure was used, and the reflux time was varied to determine what effect this variation had on the removal. Reflux times of 0, 15, 30, 60, 90, and 120 minutes were used. The dosages and the pH range were the same as those used in the dosage test.

The results of this test are shown in Figures 6-7, 6-8, 6-9, 6-10, 6-11 and 6-12 where the percent pesticide removed is plotted against the reflux time.

The curves show that the refluxing action does cause an enrichment of the foam and, therefore, an increase in the pesticide removal. This removal tends to increase until the 60 minute reflux time is reached, for times greater than this the curves tend to level off. With this refluxing action, a desired pesticide removal can be produced at a lower surface active agent dosage.

Study of the Effect of Repeated Dosing Upon the Pesticide Removal

This portion of the investigation was directed toward determining

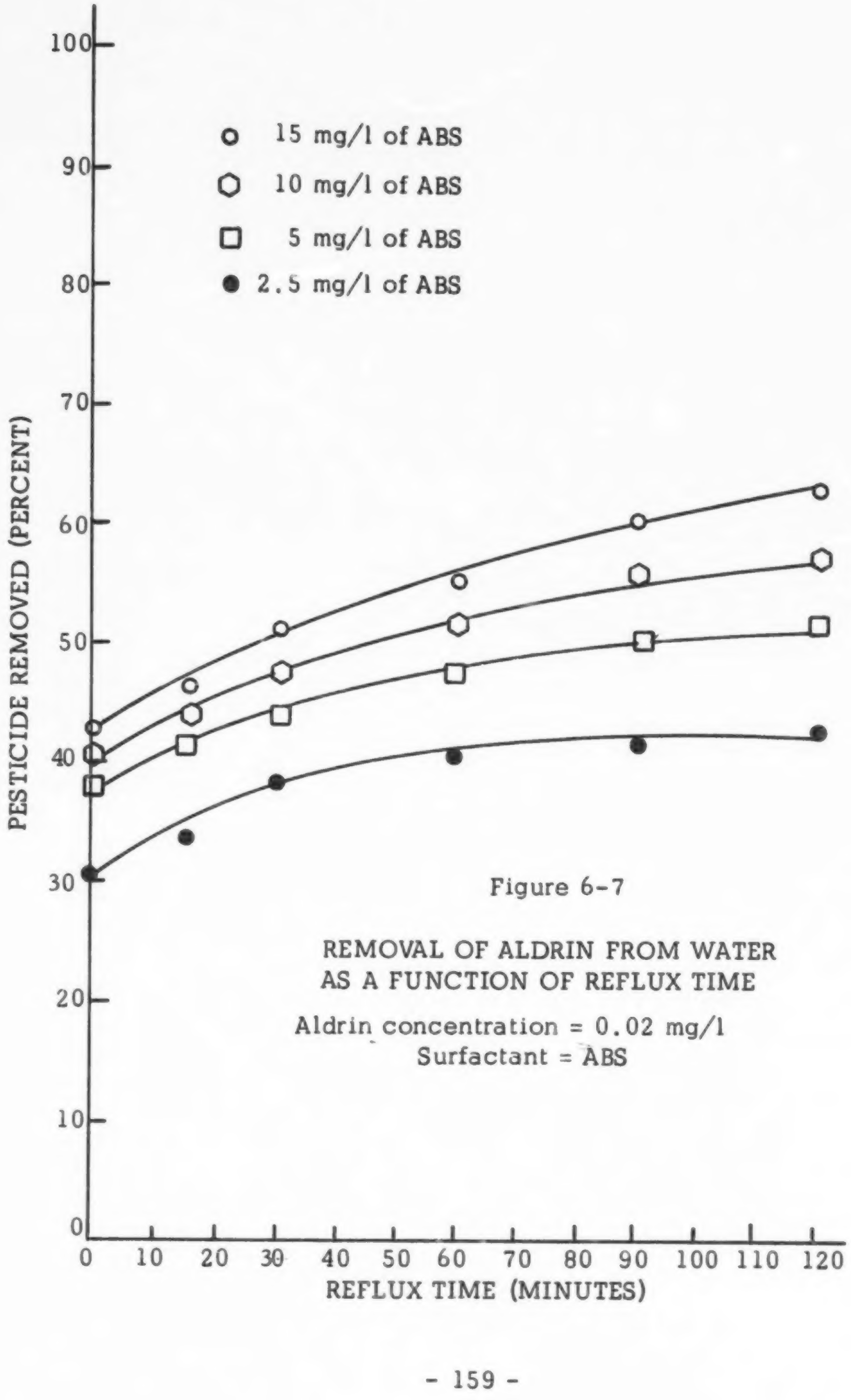


Figure 6-7

REMOVAL OF ALDRIN FROM WATER AS A FUNCTION OF REFLUX TIME

Aldrin concentration = 0.02 mg/l
Surfactant = ABS

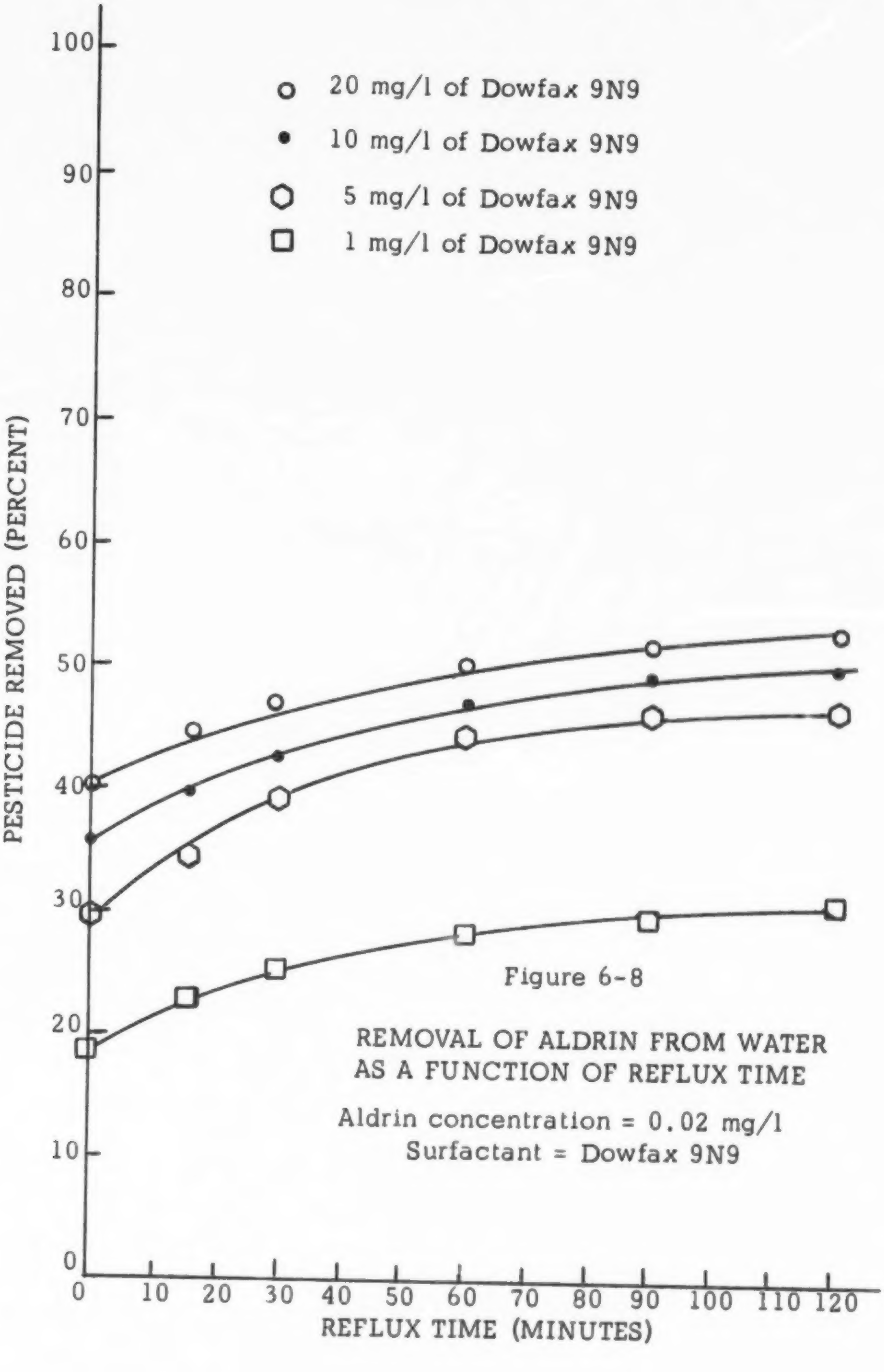


Figure 6-8

REMOVAL OF ALDRIN FROM WATER AS A FUNCTION OF REFLUX TIME

Aldrin concentration = 0.02 mg/l
Surfactant = Dowfax 9N9

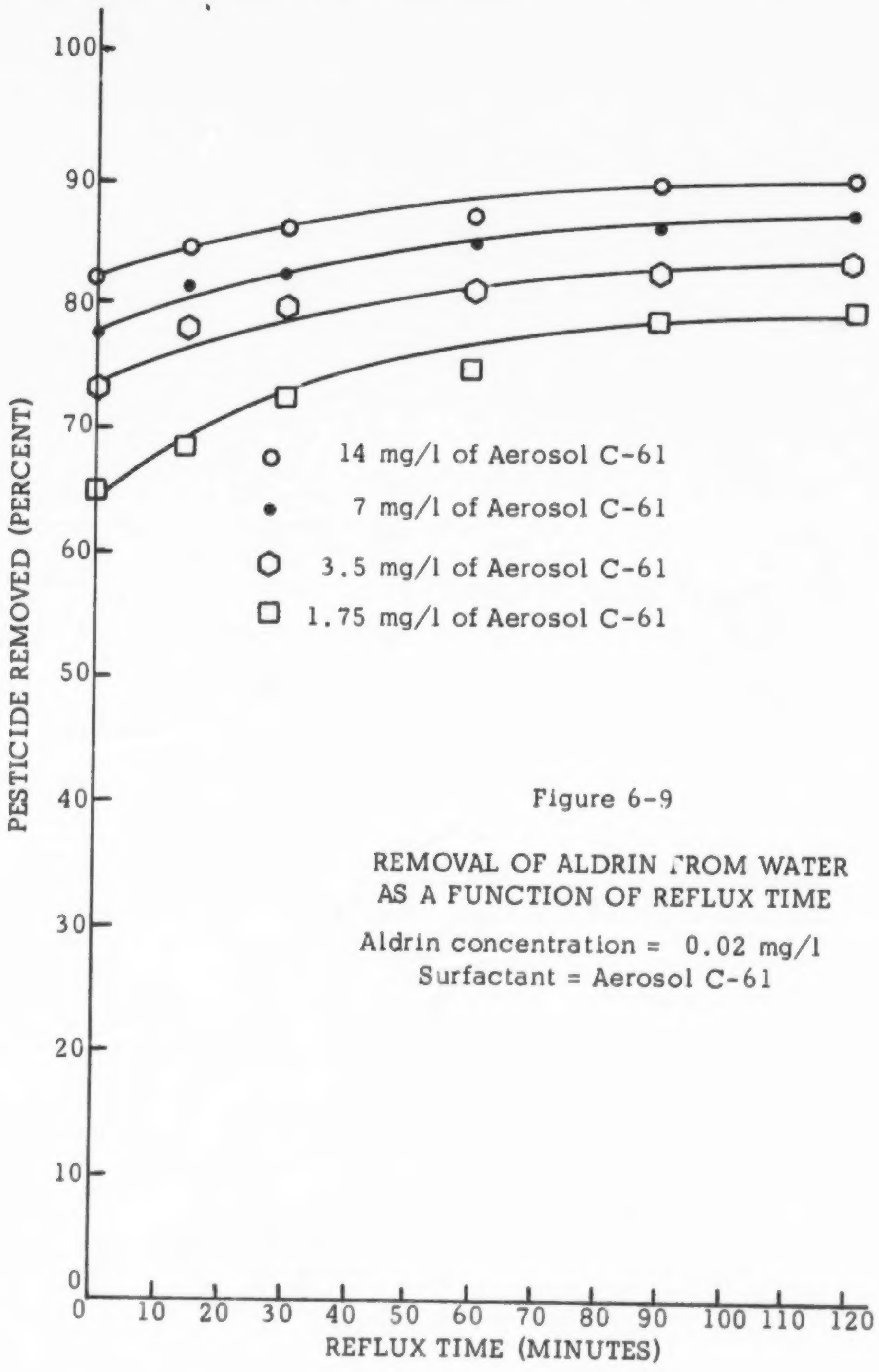


Figure 6-9

REMOVAL OF ALDRIN FROM WATER
AS A FUNCTION OF REFLUX TIME

Aldrin concentration = 0.02 mg/l
Surfactant = Aerosol C-61

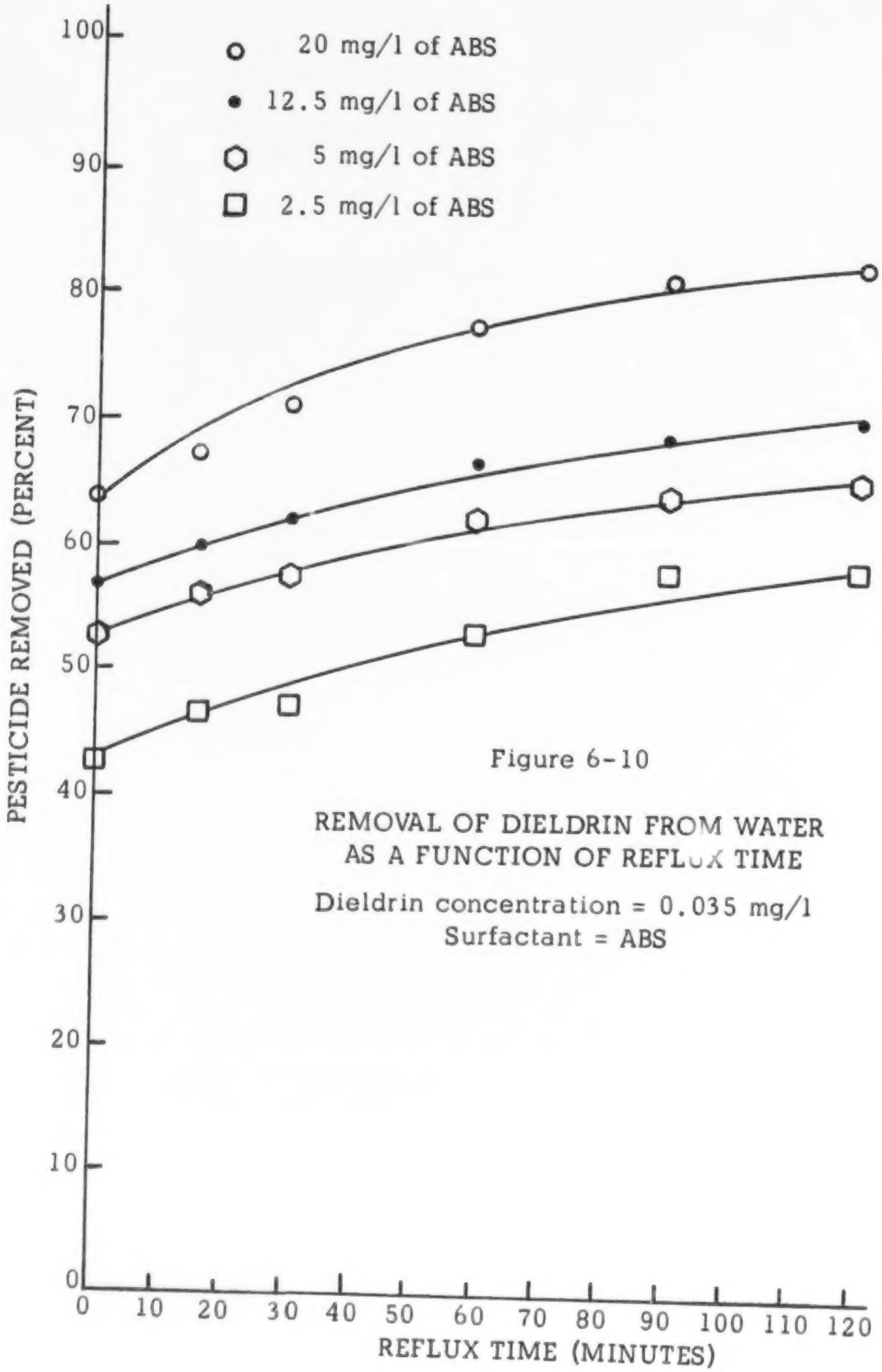


Figure 6-10

REMOVAL OF DIELDRIN FROM WATER AS A FUNCTION OF REFLUX TIME

Dieldrin concentration = 0.035 mg/l
Surfactant = ABS

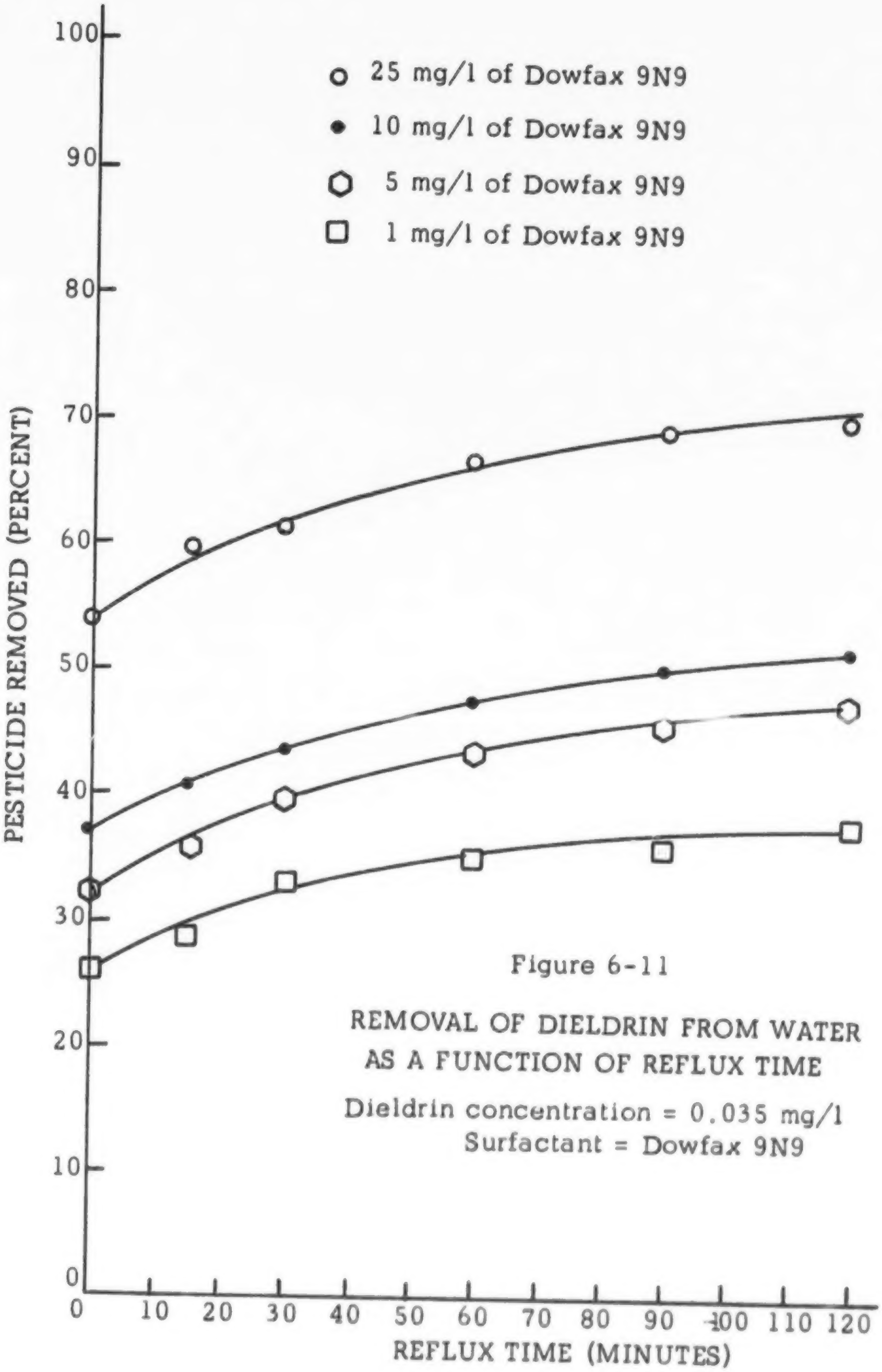


Figure 6-11

REMOVAL OF DIELDRIN FROM WATER AS A FUNCTION OF REFLUX TIME

Dieldrin concentration = 0.035 mg/l
Surfactant = Dowfax 9N9

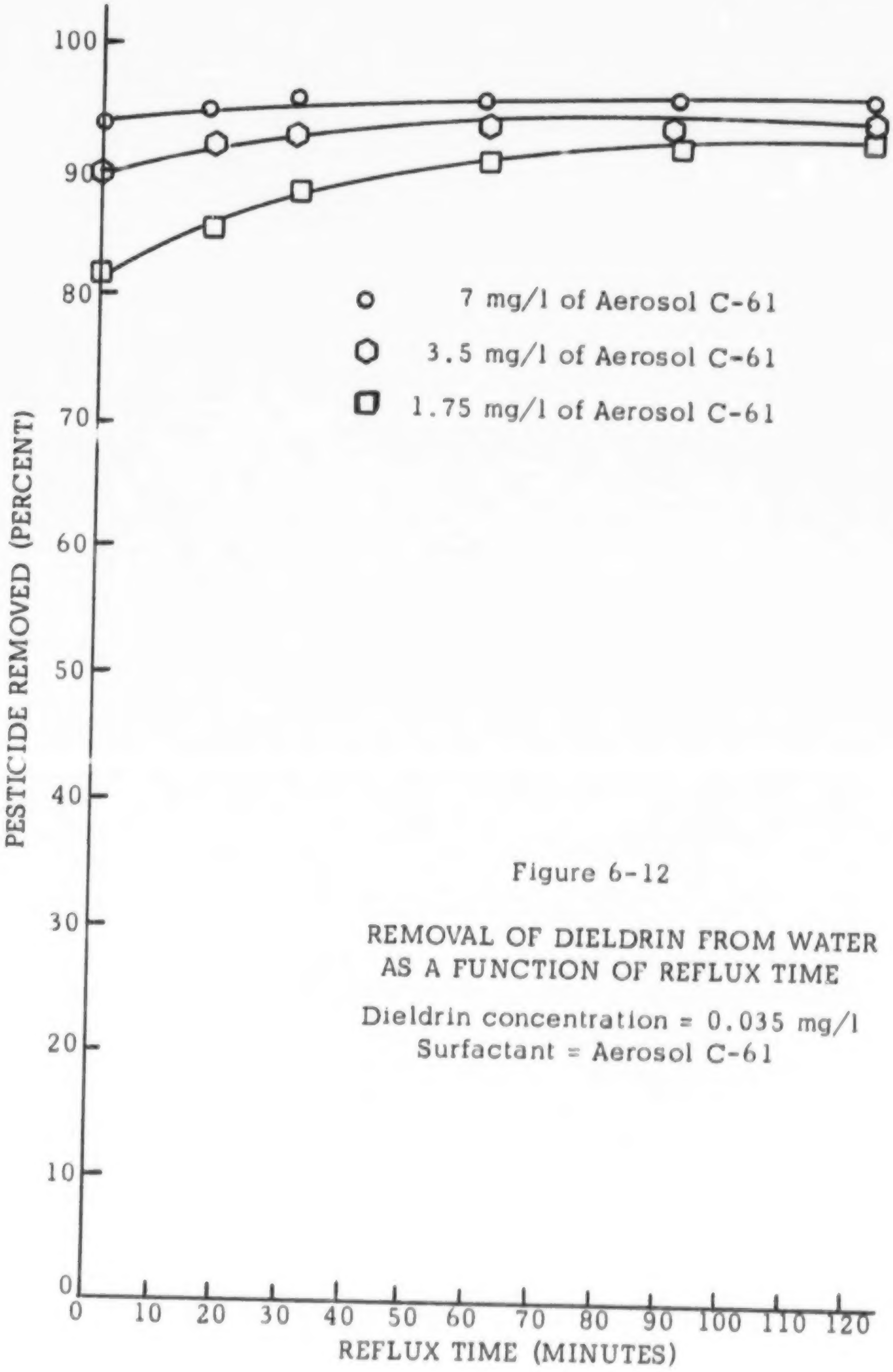


Figure 6-12

REMOVAL OF DIELDRIN FROM WATER AS A FUNCTION OF REFLUX TIME

Dieldrin concentration = 0.035 mg/l
Surfactant = Aerosol C-61

the effect of repeated dosing upon a single solution sample. The dosages used were 10 mg/l of Dowfax 9N9, 10 mg/l of ABS, and 2.5 mg/l Aerosol C-61 for both pesticides. A reflux time of one hour was used, and the pH of the solution was maintained between 6.5 and 7.5. Each pesticide solution sample was dosed, refluxed and foamed three times with each of the three surface active agents. The results of these tests are shown in Table 6-2.

TABLE 6-2

CUMULATIVE PESTICIDE REMOVED

	Aldrin			Dieldrin		
Dose No.	1	2	3	1	2	3
Surface Active Agents						
10 mg/l of Dowfax 9N9	37%	57%	64%	40%	75%	86%
10 mg/l of ABS	53%	65%	71%	52%	77%	89%
2.5 mg/l of Aerosol C-61	65%	80%	83%	83%	95%	97%

These results indicate that a higher percent removal can be obtained using this repeated dosage principle than could be obtained with a single dose three times as large. It is realized however that, theoretically, a minute portion of the pesticide will always remain in the solution no matter how many times it is dosed.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The following summary and conclusions are separated by chapters, for ease of reference.

Chapter III

The removal of pesticides from water by aeration was found to be a significant factor. There was considerable variation in the extent of loss through aeration, with dieldrin being removed almost 100 percent over the temperature range tested. The chlorinated hydrocarbon pesticides, aldrin, dieldrin, DDT, and BHC were all removed by aeration to some significant extent, but the chlorinated hydrocarbon 2,4,5-T showed no removal at all, nor did captan. It was determined that the temperature was a factor in the length of time required to reach maximum removal but not a factor in maximum removal.

The volatilization of dry pesticides at temperatures of 20°C, 30°C, and 40°C was studied. The pesticides studied, in the order of the most volatile to the least volatile, were heptachor, aldrin, lindane, dieldrin, endrin, DDT, captan, and 2,4,5-T. 2,4,5-T over the period of 100 days and the temperature range of 20°C to 40°C exhibited no valatilization. This, along with the data gathered on aeration, would indicate that 2,4,5-T is a very stable compound over the prescribed test ranges. The other pesticides tested over the period of 100 days, varied from a 1 percent to a 75 percent loss in weight.

Chapter IV

The removal of pesticides from water by chemical coagulation alone was found to be ineffective. Alum coagulation tests were performed with DDT, aldrin, dieldrin, captan, and BHC. The dosage of alum was varied from 0.02 to 1.0 grams/liter and the hardness of the samples was varied from 10 ppm to 250 ppm ($CaCO_3$). It was determined that the varying dosage and hardness had little or no effect upon removal. In the case of DDT, the removal did vary with hardness but not significantly. The removal of malathion by chemical coagulation and various additives was studied. It was determined that alum and ferric sulfate coagulation were ineffective in removing malathion. Several coagulant aids were used but, with the exception of one, all proved ineffective. One, Wisprofloc 20, increased the removal to 20 percent, which is not considered to be sufficient to be used as a treatment method. The most effective process used in conjunction with chemical coagulation was coagulation with alum supplemented with activated carbon which produced a removal of 44 percent. The removal of malathion was significantly less with this process than with activated carbon alone due to the fact that a relatively smaller amount of carbon was used.

Chapter V

The removal of pesticides from water by adsorption with activated carbon was determined to be the most effective of the methods tested. In relation to malathion the maximum removal was near 100 percent. The use of activated carbon in batch type treatment to remove low concentrations of malathion from water is relatively expensive. Approximately 4,000 pounds of carbon would be required to effect a 99 percent removal of 100 mg/l of malathion from 1 million gallons of water with a four hour contact time. It was determined that malathion adsorption on carbon is greater in more alkaline solutions than acid, and that the rate of adsorption decreases as the concentration of malathion in solution decreases.

The removal of 2,4-D from water by adsorption proved to be effective as a 90 percent removal of 2,4-D from a solution containing 100 ppm was accomplished by 100 mg/l of carbon. The removal of 2,4-D by carbon was greater at a lower pH than at a higher pH. The rate of adsorption by activated carbon decreased as the concentration of 2,4-D in solution decreased, as was the case with malathion. Two types of carbons were tested, animal and vegetable, and it was determined that the carbons of vegetable origin have a higher adsorptive capacity. Tests with differing particle sizes of carbons indicated that as the particle size decreased adsorption increased. This would be expected as the decrease in size would increase surface area.

The removal of aldrin, dieldrin, and DDT from water by activated carbon also proved effective. The factors investigated which affect the removal of aldrin, dieldrin, and DDT, by activated carbon were pH, time, and carbon dosage. pH values in the range from 5 to 9 were determined to have no effect on adsorption rate, but values below 4 accomplished removal of the pesticides from water without the use of activated carbon. Rapid initial rates of adsorption were observed with carbon dosages of 5 mg/l to 1 00 mg/l, but at dosages above 100 mg/l a gradual increase was observed. After one hour, relatively little additional removal of any of the pesticides occurred.

The removal of aldrin, dieldrin, DDT, 2,4-D, BHC, captan, and 2,4,5-T by adsorption with clays showed that some removal of dieldrin, aldrin, DDT, and BHC could be expected. The effectiveness of the removal was not as outstanding as that with activated carbon as the percent removed varied from 20 to 50 percent. Captan and 2,4,5-T were removed to the extent of approximately 5 to 10 percent. Although these removals are comparatively low, in natural circumstances, the total removal over a long period of time could be highly significant.

Chapter VI

Studies on the removal of aldrin and dieldrin from water by the use of surface active agents to produce a foam demonstrated that this process might be of value as a treatment method. The amount of removal accomplished by foaming with a given dose of surface active agent increased as the pH decreased. Of the three types of surface active agents tested, cationic, anionic, and nonionic, the cationic effected greater than 90 percent removal of both aldrin and dieldrin. As the dosage of surface active agent was increased the removal of pesticide increased rapidly through the lower dosages but tended to level off at the larger doses. A reflux action of 60 minutes was found to increase removal, but after this period no significant additional removal was observed. Repeated dosing with small amounts of surface active agents effected a greater removal than a single large dose of the same total quantity.

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